

3.

For an anion/cation balance, Mn was assumed to have a valence of 2, and iron a valence of 3. Calculations gave the following:

<u>CATIONS</u>	<u>FILTER 803</u>		<u>FILTER 805</u>	
	<u>Wt., <math>\mu</math>g</u>	<u><math>\mu</math>Equiv.</u>	<u>Wt., <math>\mu</math>g.</u>	<u><math>\mu</math>Equiv.</u>
Mn	10	0.4	12	0.4
Fe	45	2.4	66	3.6
Zn	330	10.1	380	11.6
Ca	210	10.5	240	12.0
Ba	520	7.6	580	8.5
CATIONS, TOTAL $\mu$ Equiv		31.0		36.1

<u>ANIONS</u>	<u>FILTER 803</u>		<u>FILTER 805</u>	
	<u>Wt., <math>\mu</math>g</u>	<u><math>\mu</math>Equiv.</u>	<u>Wt., <math>\mu</math>g.</u>	<u><math>\mu</math>Equiv.</u>
Cl <sup>-</sup>	3,990	113	1,990	56
SO <sub>4</sub> <sup>=</sup>	30	0.6	20	0.4
ANIONS, TOTAL $\mu$ Equiv		113.6		56.4

The Mn and S found were compared to the amounts in the gasoline burned. For these calculations, the following were used:

1. 2 Gallons of gasoline burned (20.5 mpg, for the 41 miles).
  2. Gasoline density of 0.74 Kg/liter (typical for Howell EEE). The 2 gallons is about (2)(3.78 liters/gallon)(0.74 Kg/liter) = 5.59 Kg.
  3. Sulfur concentration 0.0036 % (from conversation with Reineman). This is equivalent to 0.036 gram of sulfur per Kg. of gasoline. The 2 gallons of gasoline would have contained (5.59 Kg)(0.036 g sulfur/Kg = 0.20 g of sulfur. Conversion of this to sulfate would give 0.60 g. of sulfate.
  4. Mn concentration 1/32 gram per gallon. The 2 gallons of gasoline would have contained 1/16 gram (0.063 gram) of manganese.
- Tunnel sample conditions (from conversation with Reineman):
- A. Total flow 320 SCFM
  - B. Sample flow 25 liters/min. (0.88 SCFH).
  - C. Ratio of total to sampled flow was 320/0.88 = 364 to 1.
5. The percent recovered was calculated from:

$$\text{Percent Recovered} = \frac{(\text{Wt on Filter})(364)(100)}{\text{Wt. Burned in the 2 Gal.}}$$

	<u>FILTER 803</u>	<u>FILTER 805</u>
Percent Mn Recovered	5.8 %	6.9 %
Percent S recovered	1.8 %	1.2 %

Since the elements found on the filters are not typical components of gasoline, motor oil was considered as a possible source. Information from our St. Louis Labs gives "typical" motor oil concentrations of Ca as 0.13 Wt. %, Zn as 0.1 Wt. %, a trace of chloride (from ashless dispersant), and no Ba. Thus, gasoline engine combustion products cannot be the source of the material on the filters.

These materials are more consistent with diesel emissions. The EPA - Ann Arbor test tunnel has been used for diesel particulate testing since 1984 without having been cleaned (Reineman). Diesel particulate emissions are typically much larger than those from a gasoline engine.

By mass spectrometry, all the samples of the filter extracts, including the extract of the blank filter contained aliphatic hydrocarbons with fragment ion from C<sub>3</sub> through C<sub>12</sub> (M/z 43, 57, 71, 83, 97, 111, etc.). Other types of compounds observed in all the extract samples were phthalate esters (149, 267), aliphatic esters (256, 284, etc), aromatic ethoxylates (311, 355, 399, etc.), and poly dimethyl silicones (355, 429, 503). Exact mass measurements were made to confirm the compounds present in the extract samples.

The samples of the extracts from the primary filters (803-B and 805-B) showed greater amounts of poly dimethyl silicones, even though these compounds were present in the extract of the blank filter. The mass spectra are attached.

Lack of a good sodium analysis (the filter matrix was fiberglass, giving high levels in all extracts) complicates the mass and anion/cation balances. However, what was collected on these filters does not seem to be consistent with typical automotive emissions. Our results do seem to be consistent with those obtained by Bruce Kolowich. From conversations with Marty Reineman, Bruce has found that the material on similar filters was water soluble inorganics.

ILS/cd  
Attachment

I. L. Smith

cc: Distribution

18 December  
1990

IKE,

The filters were loaded using a Chevrolet Caprice, 4.0L, V-8, 1990 MY fueled with the same MMT fuel used for previous EPA tests. Dynamometer set conditions were 4500 lbs IW, 8.6 actual horsepower at 50 mph.

2 sets of filters were collected, each set included a primary and secondary filter. The test consisted of an unsampled LA-4 warmup, followed by 2 sampled HFETs. No LA-4 warmup was run for the second set, just the 2 HFETs

First set:

Filter 803 primary  
Filter 804 secondary

TOTAL WT OF  
PARTICULATE  
COLLECTED

0.005518g  
0.000227g

Second set:

Filter 805 primary  
Filter 806 secondary

0.003366g  
0.000171g

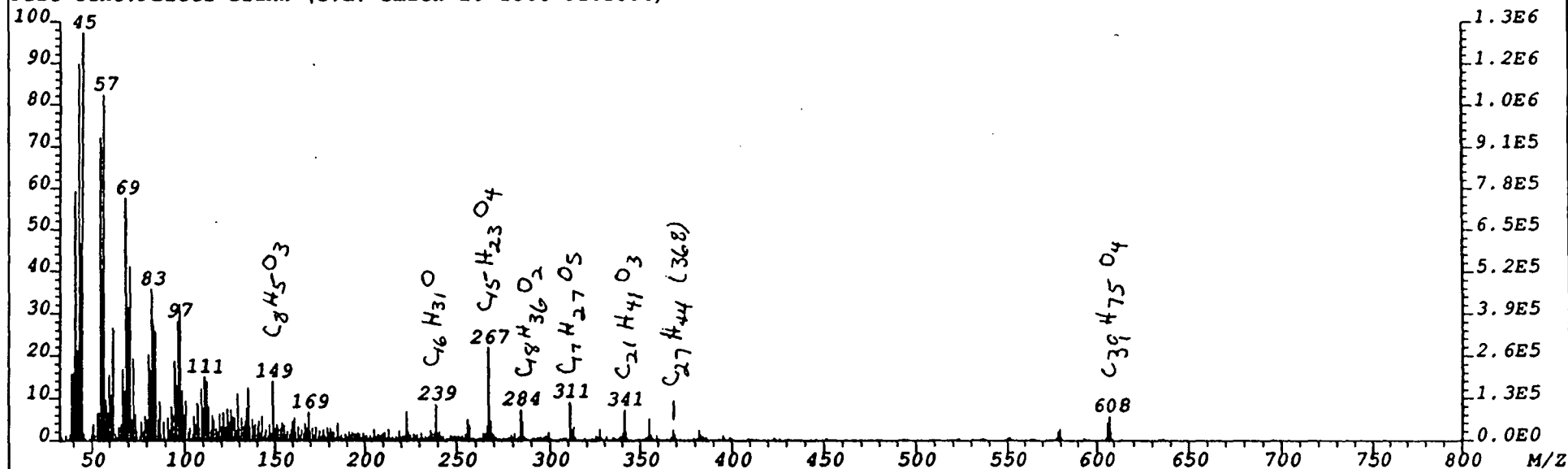
Exhaust emissions were not collected, nor were particulate emissions calculated in g/mi. A nominal 23 l/min flowrate was maintained until the end of the second HFET when the filter loaded with particulate and it was no longer possible to achieve the 23 l/min flowrate.

Marty Reneman  
313 668-4430

File:1500ILS01 Ident:4 24 Mer Def 0.25 Acquired:11-FEB-91 09:30:44

70SE Ionization:EI+ Function:Magnet

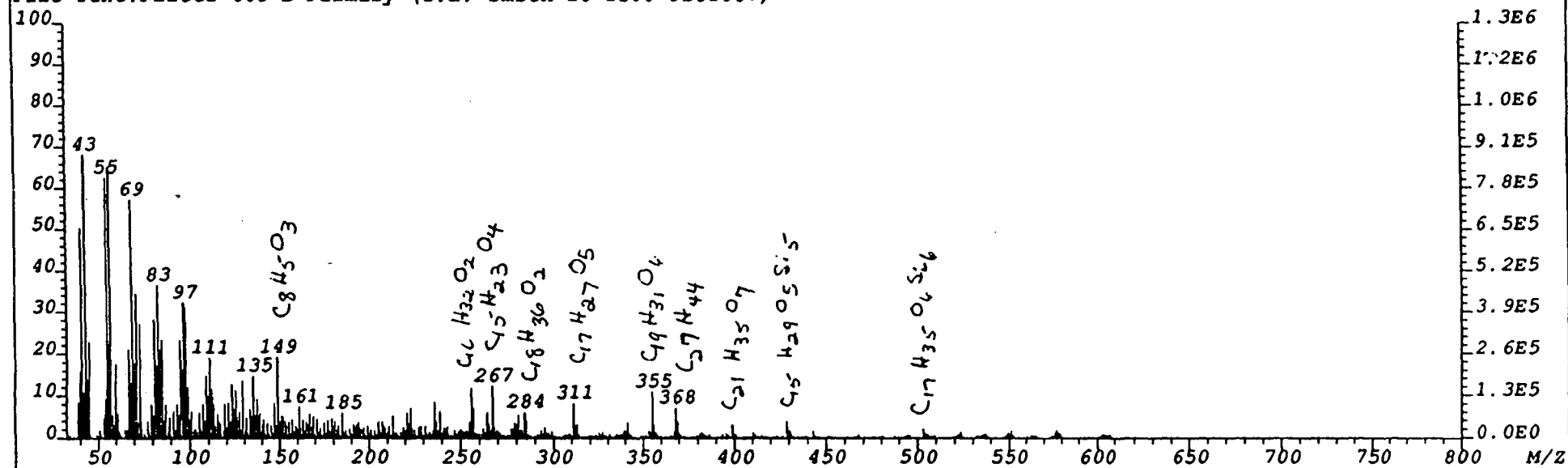
File Text:Filter Blank (I.L. Smith 20-1500 9101004)



File:1500ILS04 Ident:4 24 Mer Def 0.25 Acquired:11-FEB-91 13:32:25

70SE Ionization:EI+ Function:Magnet

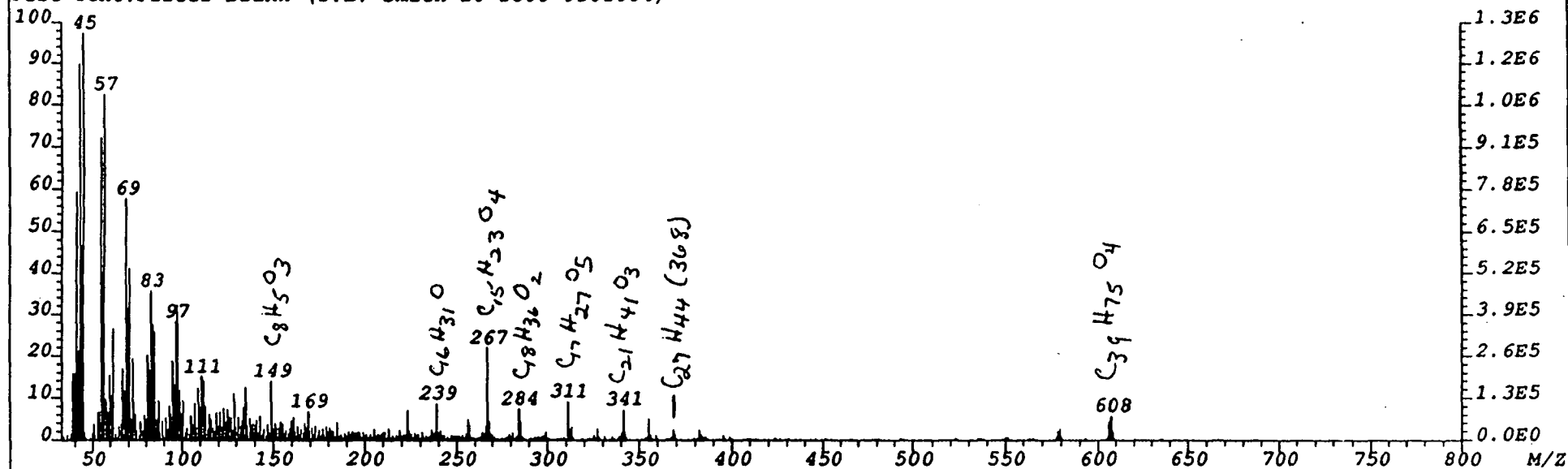
File Text:Filter 805-B Primary (I.L. Smith 20-1500 9101007)



File:1500ILS01 Ident:4 24 Mer Def 0.25 Acquired:11-FEB-91 09:30:44

70SE Ionization:EI+ Function:Magnet

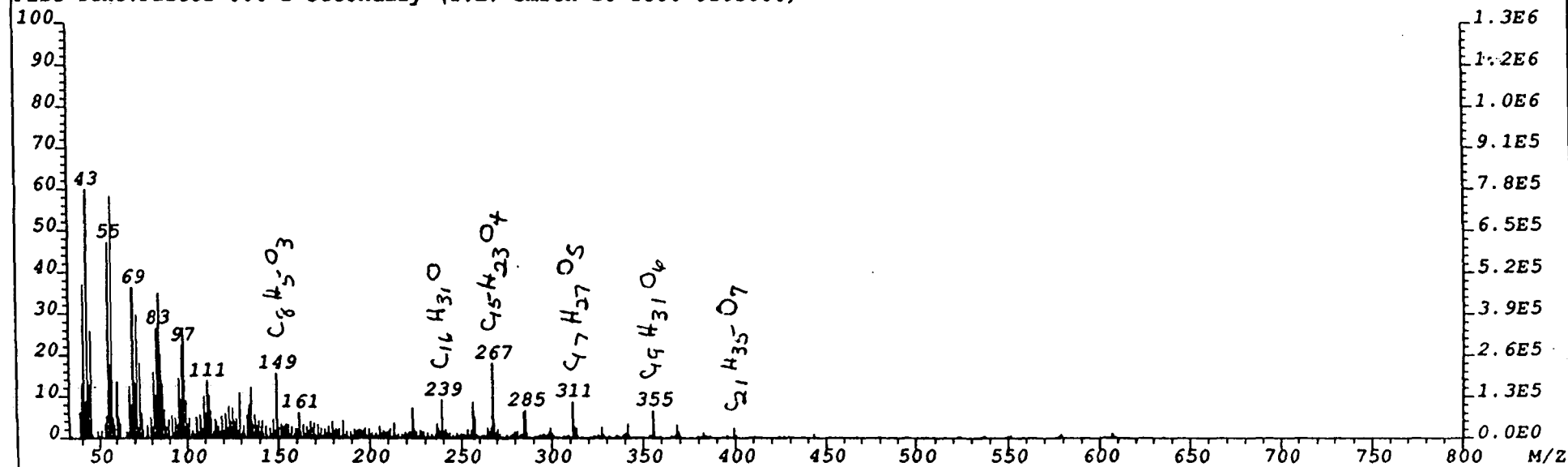
File Text:Filter Blank (I.L. Smith 20-1500 9101004)



File:1500ILS05 Ident:3 24 Mer Def 0.25 Acquired:11-FEB-91 14:56:29

70SE Ionization:EI+ Function:Magnet

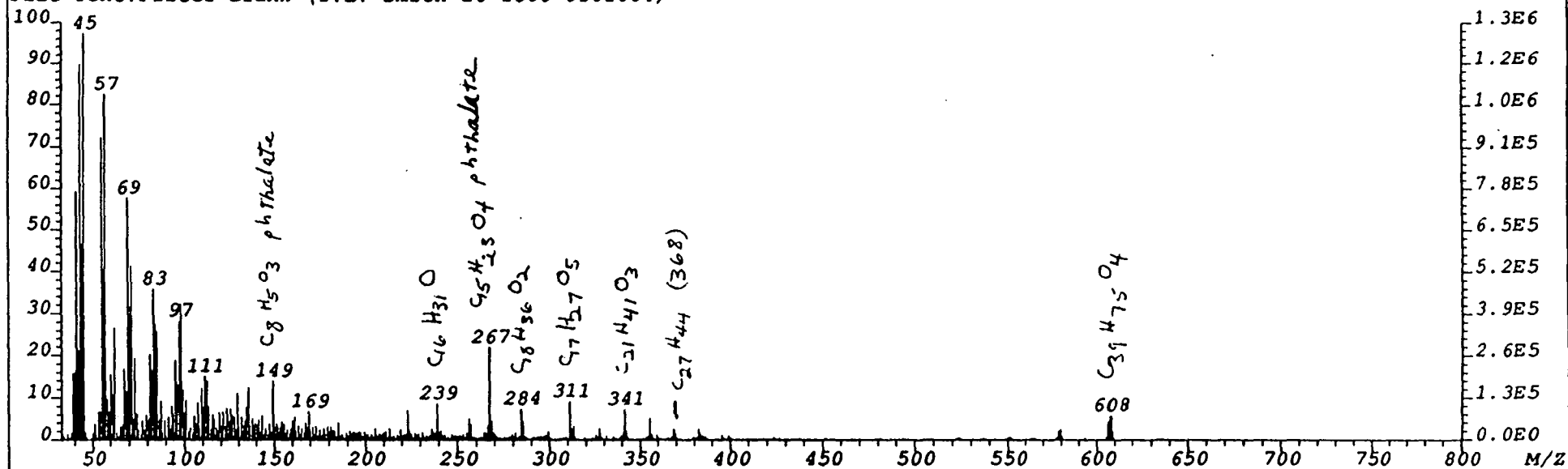
File Text:Filter 806-B Secondary (I.L. Smith 20-1500 9101008)



File:1500ILS01 Ident:4\_24 Mer Def 0.25 Acquired:11-FEB-91 09:30:44

70SE Ionization:EI+ Function:Magnet

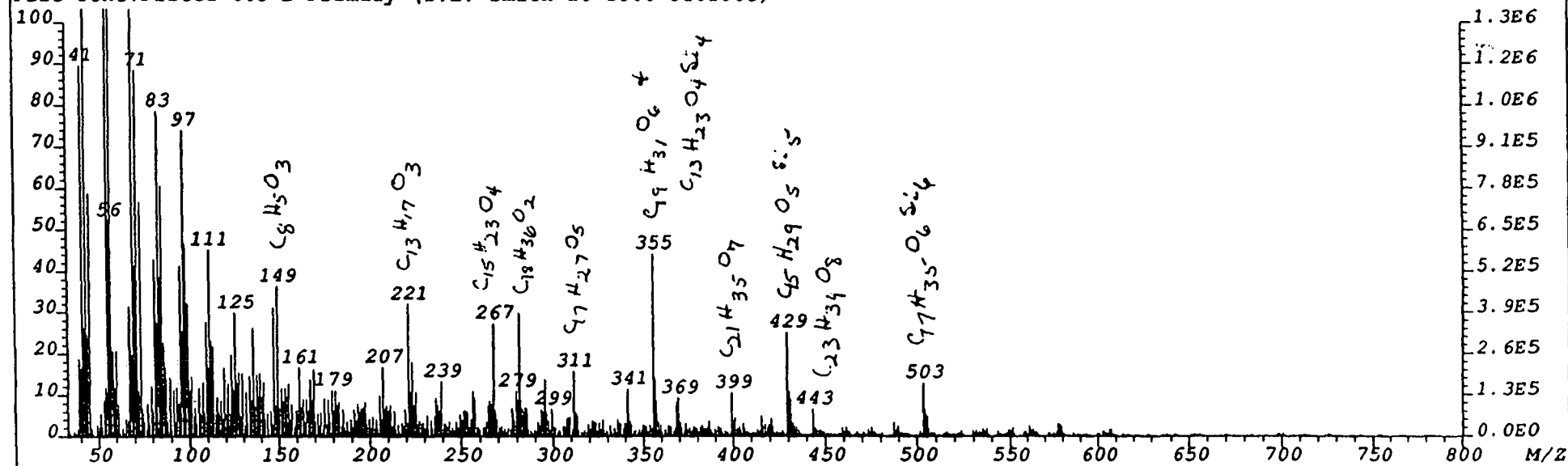
File Text:Filter Blank (I.L. Smith 20-1500 9101004)



File:1500ILS02 Ident:4\_24 Mer Def 0.25 Acquired:11-FEB-91 11:04:48

70SE Ionization:EI+ Function:Magnet

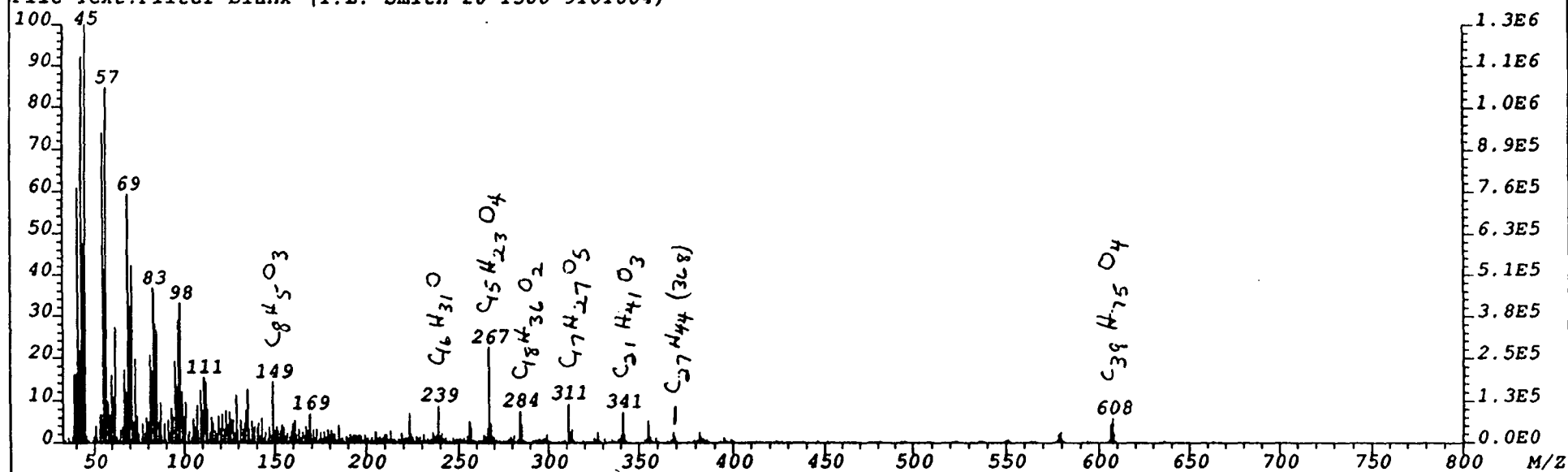
File Text:Filter 803-B Primary (I.L. Smith 20-1500 9101005)



File:1500ILS01 Ident:4 24 Mer Def 0.25 Acquired:11-FEB-91 09:30:44

70SE Ionization:EI+ Function:Magnet

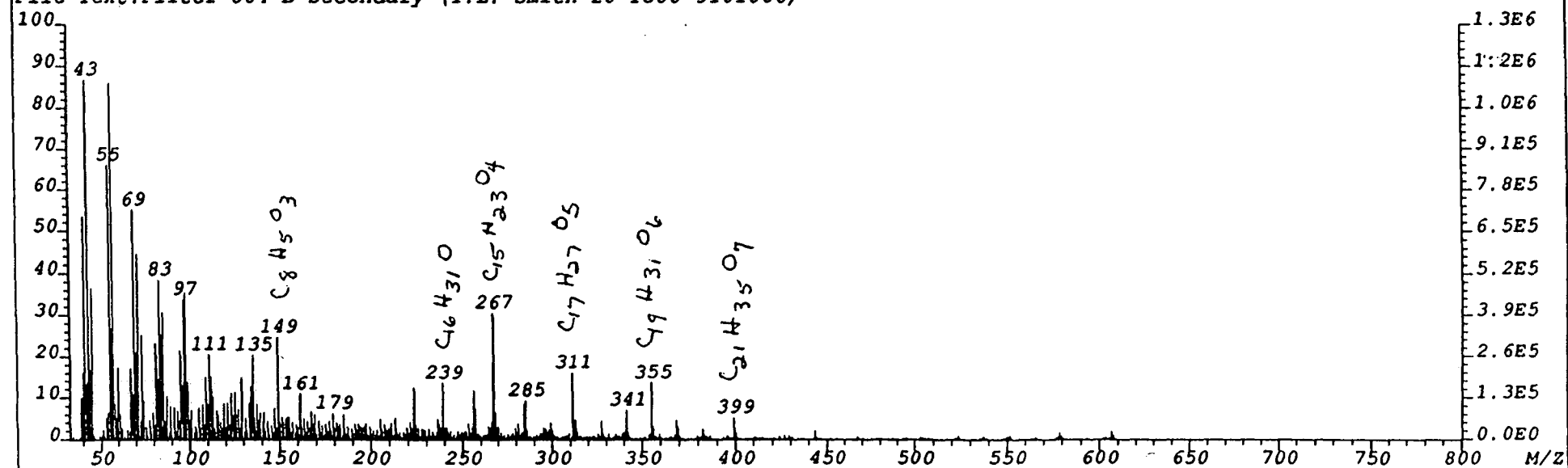
File Text:Filter Blank (I.L. Smith 20-1500 9101004)



File:1500ILS03 Ident:3 24 Mer Def 0.25 Acquired:11-FEB-91 12:32:58

70SE Ionization:EI+ Function:Magnet

File Text:Filter 804-B Secondary (I.L. Smith 20-1500 9101006)





## ANALYSIS OF EPA TEST FUEL

### I. INTRODUCTION

As part of EPA's assessment of Ethyl Corporation's ("Ethyl") HiTEC 3000® Performance Additive ("the Additive"), EPA initiated two limited, ad hoc emission test programs: one extending from August to October 1990 (the "August-October 1990 test") and a second one extending from March to May 1991 (the "March-May 1991 test"). The results of this testing (reported in Appendices 2 and 5) showed higher hydrocarbon ("HC") and particulate matter emissions than any emission testing completed by Ethyl (see, e.g., Appendices 4 and 5), or that were reflected in the joint EPA/Ethyl emission correlation test program (see Appendix 3).<sup>1/</sup>

As part of Ethyl's efforts to determine why the limited EPA test results differed from all other test results, Ethyl undertook the chemical and emission tests described below. The results of these tests show that the EPA test fuel found in the tank of the test vehicle used in the March-May 1991 test (a 3.3 liter Dodge Dynasty, also known as "Red Bruce") was contaminated with FREON® 12, a common chlorofluorocarbon refrigerant.<sup>2/</sup> This contamination likely occurred during the process of blending the Additive into the test fuel by the EPA Ann Arbor test laboratory.

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<sup>1/</sup> All references to appendices are to those which accompany this waiver application.

<sup>2/</sup> FREON® is a registered trademark of the DuPont Chemical Company.

-2-

Moreover, additional emission testing completed by Southwest Research Institute ("SWRI") on this same test vehicle confirms that the presence of the FREON® 12 contaminant in the test fuel dramatically affects vehicle tailpipe emissions of hydrocarbons and particulate matter. The EPA data generated using contaminated test fuel therefore do not provide the Agency with a basis upon which to question the results of Ethyl's extensive 48 car test program, the joint EPA/Ethyl emission correlation test program (see Appendix 3), or the SWRI particulate emission test program (Appendix 5).

## II. CHEMICAL ANALYSES

### A. Analysis of Particulates in the EPA Test Tunnel

In late June 1991, the EPA Ann Arbor test laboratory reported that it had found a "peculiar" deposit in the particulate test tunnel used in the August-October 1990 and March-May 1991 testing. A sample of this deposit was provided to Ethyl for chemical analysis. Energy Dispersive X-Ray Spectroscopy (EDXS) of the deposit sample showed the presence of chloride, iron, fluoride, sulfur, chromium, and nickel. X-Ray Diffraction showed ammonium chloride to be essentially the only crystalline compound present. (Not having seen nitrogen by EDXS is consistent with these XRD results. A diamond window used in the EDXS would have absorbed the nitrogen X-Rays.) X-Ray Photoelectron Spectroscopy (XPS) detected chloride, nitrogen, fluoride, carbon, oxygen, and sulfur, plus trace amounts of sodium and zinc. The XPS results showed that the sulfur was

-3-

present as sulfate. Ion chromatographic analysis gave 25%  $\text{NH}_4^+$ , 61% chloride, and 2.5%  $\text{SO}_4^{2-}$ .

The fact that the bulk of the material (about 86%) was ammonium chloride is consistent with the results of an earlier analysis of a particulate collection filter loaded by EPA in connection with the August-October 1990 testing. This earlier analysis also showed the bulk of the particulate on the filter to be chloride. See Appendix 5, Attachment 5.

B. EPA Test Fuel

Ethyl chemically analyzed a sample of the gasoline from the tank of EPA's "Red Bruce" test vehicle immediately upon receipt of the vehicle by SWRI on June 28, 1991. This vehicle had been shipped to SWRI from the EPA Ann Arbor test laboratory with gasoline in the tank containing 1/32 gram manganese per gallon of gasoline as blended by the EPA Ann Arbor test laboratory. This gasoline had been blended using Sun certification fuel from EPA-Ann Arbor's clear fuel storage tank. Analyzed by X-Ray Fluorescence (XRF), the gasoline tank sample contained 90 parts per million (ppm) chloride (equivalent to 0.25 gram of chloride per gallon). Gas Chromatography-Mass Spectroscopy (GC-MS) showed the chlorinated compound to be Dichlorodifluoromethane (FREON-12®). The GC-MS data for the Red Bruce tank fuel sample are provided in Attachments 1, 2, and 3.

Independently, clear Sun certification fuel, traceable to EPA-Ann Arbor's clear fuel storage tank, was also analyzed by XRF

-4-

and GC-MS.<sup>3/</sup> No chloride was found by XRF (<10 ppm, limit of detection). No organo-chlorine compounds were found by GC-MS.

Finally, on July 1, 1991, Ethyl requested EPA Ann Arbor to prepare a drum of Sun certification fuel containing the Additive. Ethyl supplied to EPA for blending a sample of Sun certification fuel without the Additive obtained earlier from EPA.<sup>4/</sup> EPA blended the Sun oil certification fuel containing the Additive using EPA equipment on July 1, 1991. The blend was chilled for about 20 minutes in an EPA blending tank containing an internal refrigeration system.

After EPA Ann Arbor blended the fuel, samples of the fuel with and without the Additive were analyzed by XRF and GC-MS. Acetone used to clean the cans containing the fuel samples was also analyzed by these techniques. The base fuel did not show any chloride by XRF (<10 ppm, limit of detection). About 19 ppm chloride was found in the acetone by XRF. No organo-chlorine compounds were found in either the base fuel or the acetone by GC-MS. By contrast, the fuel containing the Additive made in EPA Ann Arbor's blending equipment showed 760 ppm chloride (equivalent to 2.1 grams of chloride per gallon) by XRF. GC-MS identified the chlorinated organic in this blend as also being

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<sup>3/</sup> ECS Laboratory obtained the Sun Oil certification fuel from the EPA Ann Arbor underground storage tank in mid-June 1991. A portion of the fuel was sent to SWRI and the balance was retained by ECS. The Sun Oil certification fuel sample which was analyzed came from SWRI.

<sup>4/</sup> See supra note 2.

-5-

FREON® 12. Because FREON® 12 was present in all the EPA test fuel samples containing the Additive, it is likely that the equipment used by the EPA Ann Arbor test laboratory to blend the Additive into the test fuels is the source of the FREON® 12 contamination.<sup>5/</sup>

### III. EMISSION TESTING ON EPA'S RED BRUCE TEST VEHICLE

In addition to chemically analyzing the Red Bruce tank fuel, SWRI measured emissions from the vehicle using the EPA Sun certification tank fuel and the same procedures employed by EPA Ann Arbor in its testing. SWRI then tested the Red Bruce vehicle using Sun certification fuel containing the Additive as blended by ECS.<sup>6/</sup> The results of this additional emission testing,

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<sup>5/</sup> The sample of the Additive provided by Ethyl to EPA for testing is unlikely to be the source of the contamination because EPA obtained similar emission results using a commercially available additive containing manganese, which to Ethyl's knowledge does not contain chloride. The probability that the two independent sources of manganese would both be contaminated with a chloride compound is exceedingly small.

Moreover, EPA has indicated that the clear test fuels and the test fuels containing the Additive came from different storage tanks. All clear test fuels came from dispensers normally used for certification testing. By contrast, when fuel containing the Additive was used for testing, it came from "a fuel conditioning cart" which "contained its own refrigeration system." See Appendix 5, Attachment 1, at 1-2. As explained by EPA, "[o]nly one cart was used for all MMT containing test fuel." Id. at 2.

<sup>6/</sup> The blending process used by ECS laboratory and SWRI differs from the method used by EPA. Ethyl prepares a dilute one pint can of gasoline with a sufficient amount of the Additive to treat a 50 gallon drum. ECS and SWRI add the contents of this one pint can to the 50 gallon drum during the drum filling process. For the Sun Oil certification fuel, ECS physically blended the Additive during the drum filling process at the EPA

(continued...)

-6-

shown below, further confirm that EPA and SWRI have correlated in all pertinent respects for emissions testing (since EPA and SWRI obtain essentially the same results using EPA's contaminated fuel), and strongly suggest that the differences in HC and particulate emission measurements obtained by EPA Ann Arbor and the other independent laboratories is largely attributable to the contamination of the EPA test fuel with FREON® 12.<sup>1/</sup>

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<sup>6/</sup> (...continued)

Ann Arbor test lab when it obtained the Sun Oil certification fuel from EPA Ann Arbor.

The procedures used by ECS and SWRI for chilling prior to FTP testing also differ from those used by the EPA Ann Arbor test lab. ECS uses a two compartment cooler. Ethylene glycol is chilled and circulated in a primary container while the fuel is held in a separate secondary, leak proof container which is immersed in the chilled glycol. SWRI uses a 30 gallon container which is then placed in a cold storage room which maintains a temperature of 45° Fahrenheit. As noted above, EPA chills the fuel in a fuel conditioning cart containing its own internal refrigeration system. See supra note 4.

<sup>1/</sup> EPA also obtained manganese emissions data during the August-October 1990 tests. Contamination of the test fuel with chlorinated hydrocarbons would contribute to particulate and HC, but not manganese, emissions. Accordingly, the manganese emissions data obtained during this test program, which was consistent with the manganese emissions data from SWRI and ECS, would continue to be valid.

-7-

**TABLE 1**  
**RED BRUCE TAILPIPE EMISSIONS**  
**Sun Oil Certification Fuel w/the Additive**

**FTP Cycle<sup>8/</sup>**

<u>Lab</u>	<u>Date</u>	<u>Fuel<sup>9/</sup></u>	<u>HC</u>	<u>CO</u>	<u>NOx</u>	<u>PM</u>
EPA	6/18/91	EPA	0.449	3.618	0.635	0.068
		Blend				
EPA	6/19/91	EPA	0.441	3.325	0.691	0.067
		Blend				
SWRI	7/1/91	EPA	0.440	3.090	0.640	0.044
		Blend				
SWRI	7/2/91	EPA	0.490	3.070	0.580	0.042
		Blend				
SWRI	7/3/91	ECS	0.410	2.920	0.520	0.015
		Blend				
SWRI	7/8/91	ECS	0.400	2.950	0.460	0.006
		Blend				
SWRI	7/9/91	ECS	0.380	2.800	0.450	0.002
		Blend				

**HWFE Cycle<sup>10/</sup>**

<u>Lab</u>	<u>Date</u>	<u>Fuel<sup>11/</sup></u>	<u>HC</u>	<u>CO</u>	<u>NOx</u>	<u>PM</u>
EPA	6/18/91	EPA	0.036	0.472	0.097	0.065
		Blend				
EPA	6/19/91	EPA	0.040	0.693	0.126	0.089
		Blend				
SWRI	7/3/91	ECS	0.050	0.800	0.120	0.016
		Blend				
SWRI	7/8/91	ECS	0.040	0.780	0.130	0.006
		Blend				
SWRI	7/9/91	ECS	0.040	0.710	0.130	0.003
		Blend				

<sup>8/</sup> Federal Test Procedure

<sup>9/</sup> Indicates which laboratory blended the Additive into the test fuel.

<sup>10/</sup> Highway Fuel Economy Cycle. Because the amount of fuel in the tank of the Red Bruce vehicle as received from the EPA Ann Arbor test lab was limited, SWRI was not able to conduct HWFE and NYCC test runs on the EPA tank fuel.

<sup>11/</sup> Indicates which laboratory blended the Additive into the test fuel.

-8-

(Table 1 continued)

NYCC Cycle <sup>12/</sup>						
<u>Lab</u>	<u>Date</u>	<u>Fuel</u> <sup>13/</sup>	<u>HC</u>	<u>CO</u>	<u>NOX</u>	<u>PM</u>
EPA	6/18/91	EPA	0.530	2.287	1.302	0.036
		Blend				
EPA	6/19/91	EPA	0.941	3.214	1.641	0.049
		Blend				
SWRI	7/3/91	ECS	0.370	3.840	1.450	0.012
		Blend				
SWRI	7/8/91	ECS	0.390	5.100	1.240	0.011
		Blend				
SWRI	7/9/91	ECS	0.440	4.850	1.460	0.004
		Blend				

This conclusion is also supported by additional gaseous emission testing conducted at ECS laboratories on a Ford Crown Victoria using the Sun Oil certification test fuel that Ethyl requested EPA to blend on July 1, 1991.<sup>14/</sup> As noted above, this EPA blended test fuel, when containing the Additive, was also found to be contaminated with FREON-12®.<sup>15/</sup> The table below shows that the presence of the FREON-12® contaminant in the test fuel substantially increases HC and CO gaseous emissions.<sup>16/</sup>

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<sup>12/</sup> New York City Cycle

<sup>13/</sup> Indicates which laboratory blended the Additive into the test fuel.

<sup>14/</sup> See supra at 3-4.

<sup>15/</sup> See supra at 4.

<sup>16/</sup> The ECS Laboratory and the EPA Ann Arbor test lab have been shown to correlate on gaseous emissions measurements. See Appendix 3.



-9-

TABLE 2

**FORD CROWN VICTORIA TAILPIPE EMISSIONS**  
**FTP<sup>17/</sup> - Sun Oil Certification fuel w/the Additive**  
**ECS Laboratories**

<u>DATE</u>	<u>FUEL<sup>18/</sup></u>	<u>HC</u>	<u>CO</u>	<u>NOx</u>
6/18/91	ECS Blend	0.267	1.150	0.763
6/19/91	ECS Blend	0.274	1.140	0.750
7/2/91	EPA Blend	0.373	1.423	0.669
7/3/91	EPA Blend	0.437	1.949	0.837
7/5/91	EPA Blend	0.526	2.169	0.668

#### IV. CONCLUSION

FREON® 12 contamination appears to explain the high particulate and gaseous emissions found with manganese containing gasoline blends at the EPA Ann Arbor test laboratory in the August-October 1990 and March-May 1991 tests. With respect to particulate emissions, combustion of FREON-12® would give hydrochloric acid and hydrofluoric acid. Since ammonia is formed in the catalyst system from nitrogen oxide reduction, ammonium chloride and ammonium fluoride would exit the exhaust system of vehicles operating on contaminated fuel, and be detected as particulate in particulate test measurements. FREON-12® contamination could also account for the composition of the particulate found on filters loaded by EPA and analyzed by Ethyl in connection with EPA's August-October 1990 tests which also showed high levels of chloride.

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<sup>17/</sup> Federal Test Procedure

<sup>18/</sup> Indicates which laboratory blended the Additive into the test fuel.

-10-

With respect to gaseous emissions, the presence of FREON-12® would likely result in poorer combustion thereby increasing gaseous emissions. This conclusion is supported by additional emission testing of a Ford Crown Victoria using contaminated EPA fuel at ECS laboratories, and is reflected in emission data from the Red Bruce test vehicle using both contaminated and uncontaminated fuel containing the Additive.

For these reasons, EPA's limited emission data using contaminated test fuel does not provide the Agency a basis to question the gaseous and particulate matter emissions data from Ethyl's extensive 48 car test program or the other emission test programs recently completed by ECS and SWRI.

# RIC-MASS CHROMATOGRAM

07/01/91 15:05:00

SAMPLE: RED BRUCE GASLINE (SMITH 9107005)

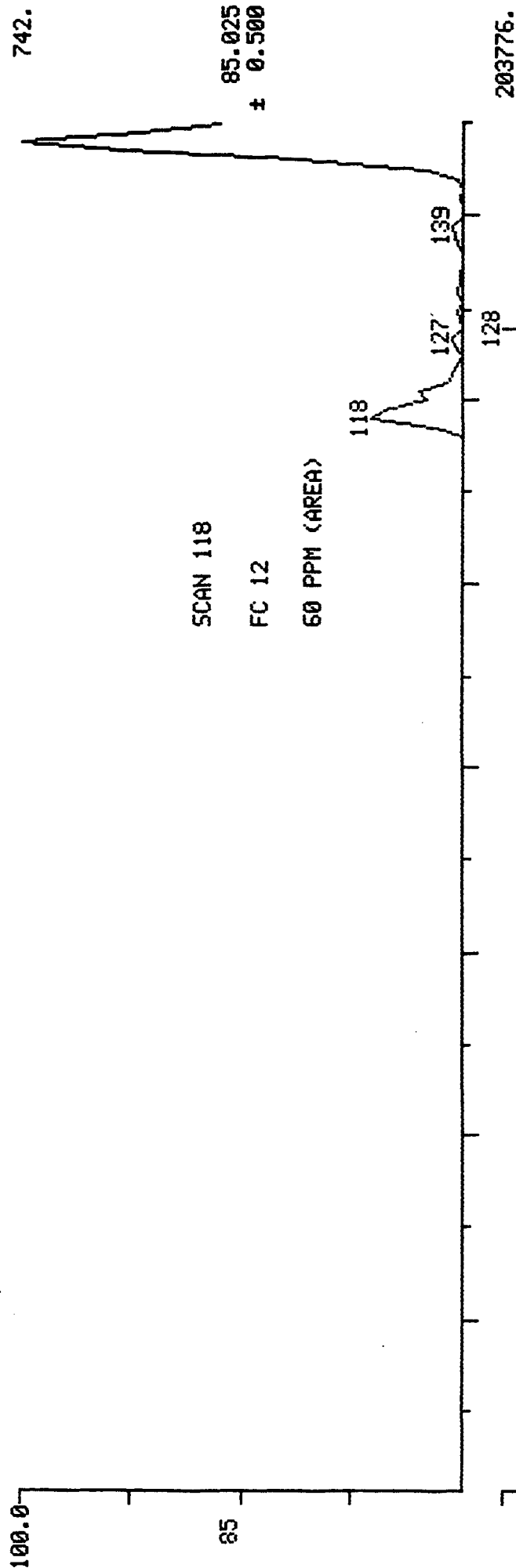
COND5.: 30M DB5 50-300010 -2MINIH

RANGE: G 1.1500 LABEL: N 0.4.0 QUAN: A 0.1.0 J 0 BASE: U 20. 3

SCANS 1 TO 150

DATA: 1500IL503 #116

CALI: CAL45 #10



SCAN 118

FC 12

60 PPM (AREA)

85.025  
± 0.500

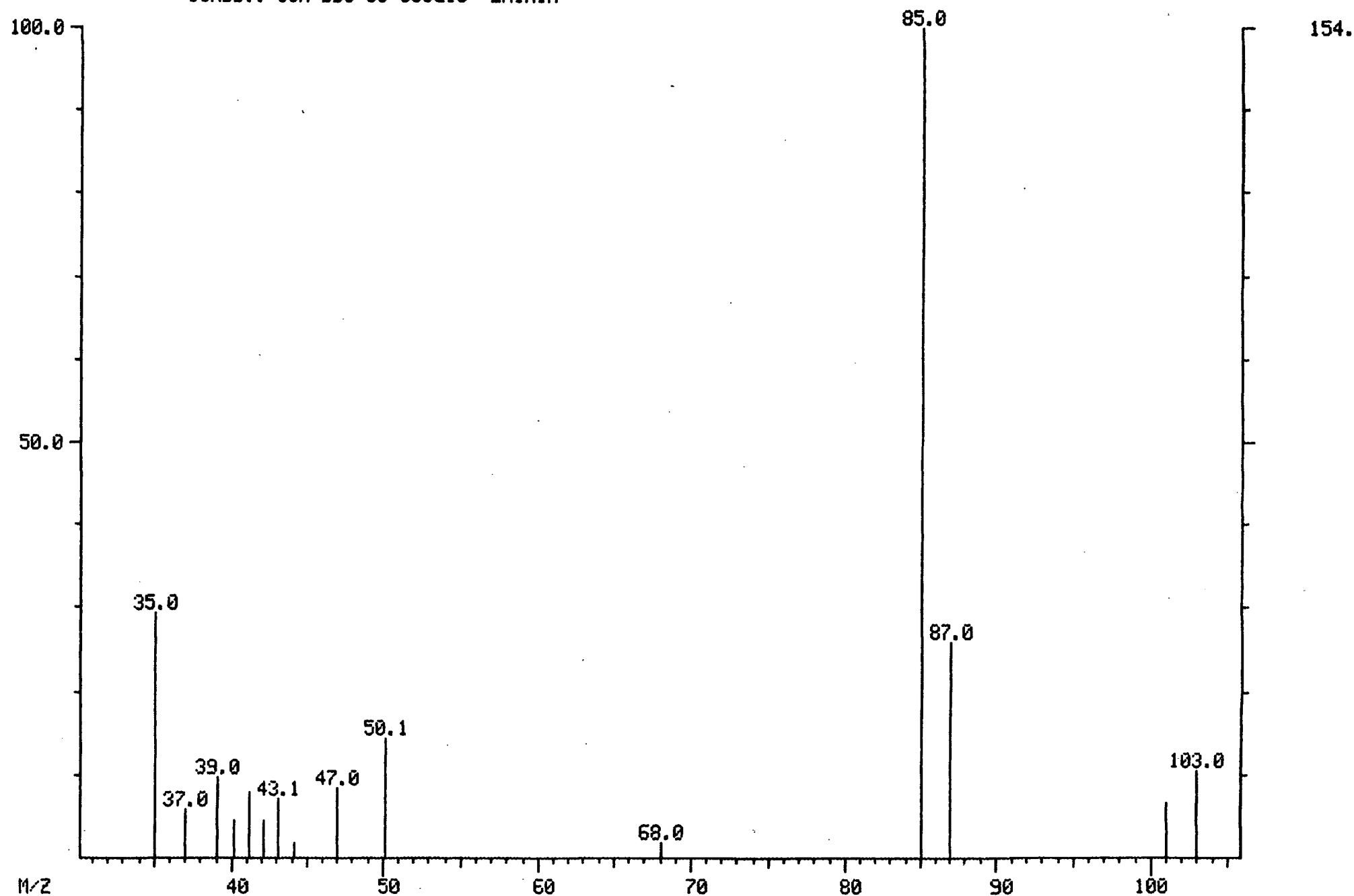
RIC

20 40 60 80 100 120 140  
0:10 0:20 0:30 0:40 0:50 1:00 1:10  
SCAN TIME

MASS SPECTRUM  
07/01/91 15:05:00 + 0:59  
SAMPLE: RED BRUCE GASLINE (SMITH 9107005)  
CONDS.: 30M DB5 50-300@10 -2MINIH

DATA: 1500ILS03 #118  
CALI: CAL45 #10

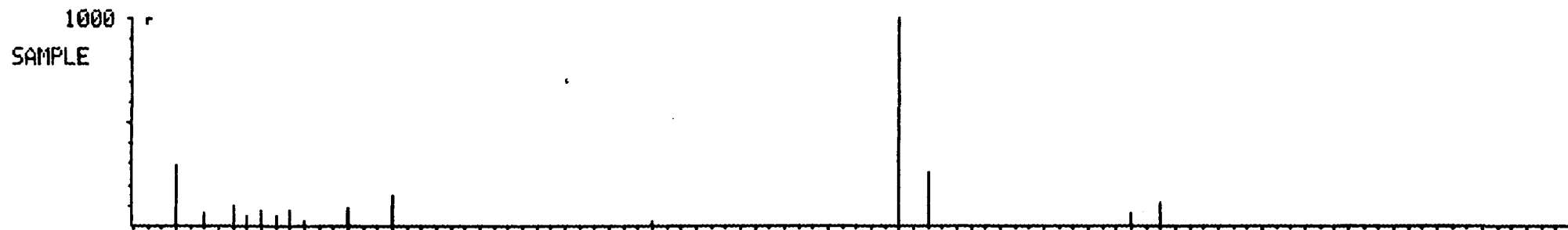
BASE M/Z: 85  
RIC: 367.



LIBRARY SEARCH  
07/01/91 15:05:00 + 0:59  
SAMPLE: RED BRUCE GASLINE (SMITH 9107005)  
CONDS.: 30M DB5 50-300@10 -2MINIH

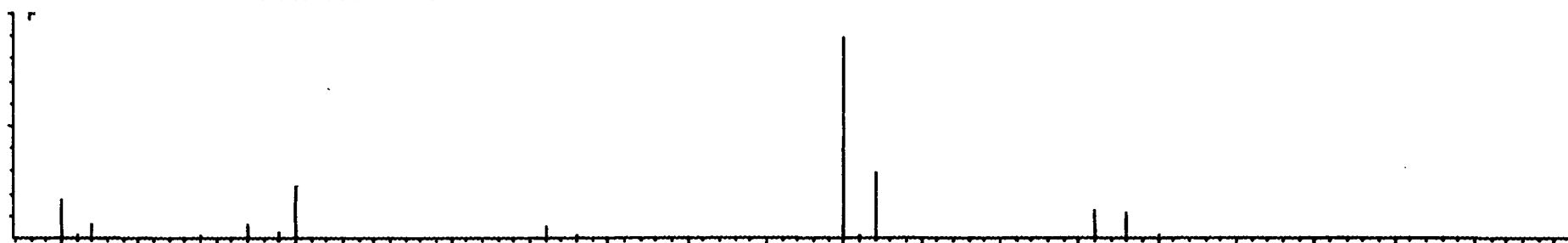
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CALI: CAL45 # 10

BASE M/Z: 85  
RIC: 366.

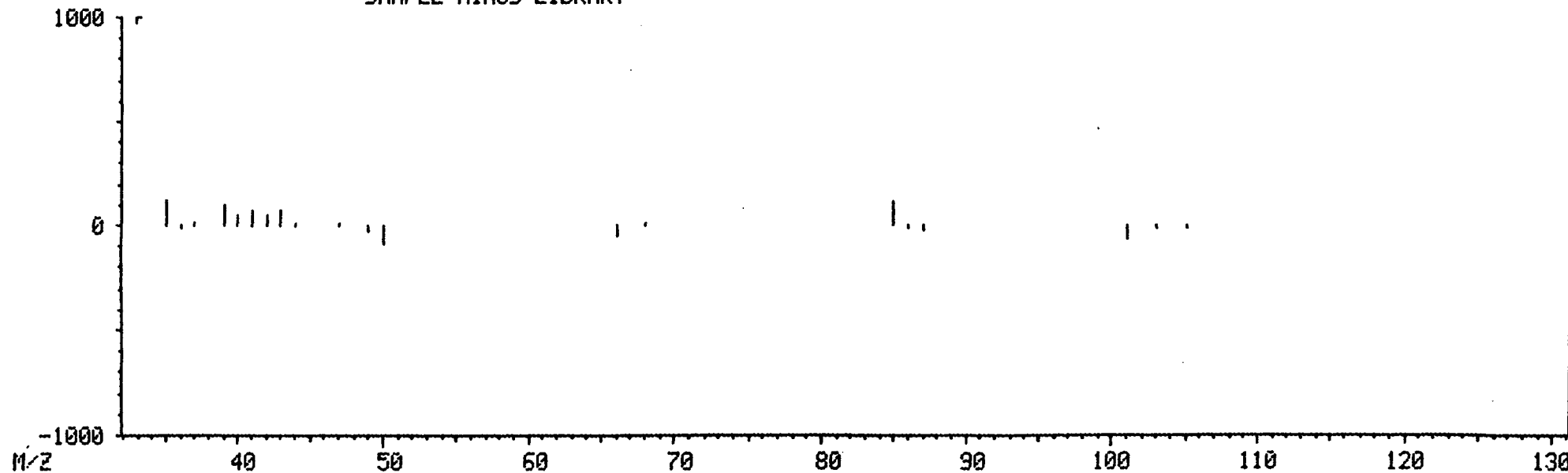


C.CL2.F2  
M WT 120  
B PK 85  
RANK 1  
# 3014  
FIT 945

METHANE, DICHLORODIFLUORO-



SAMPLE MINUS LIBRARY





UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

ANN ARBOR, MICHIGAN 48105

January 23, 1991

OFFICE OF  
AIR AND RADIATION

MEMORANDUM

SUBJECT: Particulate Measurement from Light-Duty Otto-Cycle Vehicles:  
Potential Improvements to Existing Light Duty Diesel Procedures

FROM: Carl J. Ryan, Manager  
Laboratory Projects Group, EOD

*Carl Ryan*

TO: James McCargar, Project Manager  
CB, CD

The light-duty diesel particulate procedure, in essence, is being proposed to measure particulate from Otto-cycle vehicles. This procedure appears as though it is a good starting point, but as with any procedure, there are possible areas for improvement. We have identified a number of these below. We are beginning our own investigation into these areas; however, we are seeking input from people inside or outside EPA who may have already studied these issues.

In particular, the parameters that interest us the most are the following:

1. The recommended minimum filter loading in the existing light-duty diesel particulate procedure is 0.5 mg. This criterion is intended to ensure that the quantity of particulate collected on the filter can be accurately weighed on a microgram balance. Could this level be lowered and still have acceptable test results? Maintaining the 0.5 mg level of filter loading for Otto-cycle vehicles may justify examining alternative designs to the existing diesel particulate sampling systems.

Alternatively, could the test be run using only one filter instead of three? This would increase the filter loading, but the final mass emissions might be different since the weighted mass formula could not be used. An analysis of the effect of loading all three phases of the FTP onto one filter is attached (see Attachment A). The weighted grams per mile of particulate, if one filter is used, could vary from -60% to -30% compared to using three filters for the three phases of the FTP. The difference is zero if the loading on the three filters is equal. As the loading on the three individual filters becomes more unequal, the difference in weighted mass results between the two methods becomes larger.

-2-

2. How closely should proportional sampling be controlled (i.e., what is an acceptable limit of variation in proportionality between the CVS flow rate and the particulate sample flow rate)? This will dictate the types of control systems used for achieving proportional sampling. Achieving tighter control levels may require a heat exchanger in the CVS or an electronic proportional flow controller for the particulate sample system.
3. What are acceptable temperature limits in the CVS sample zone? Retaining the 125° F maximum used for diesel testing will likely require higher dilution air flow rates for gasoline-fueled vehicles. This is because gasoline-fueled vehicles generally produce hotter exhaust gases than diesel vehicles. Increasing the dilution air flow would lower the concentration of the dilute exhaust gases and particulate, making these more difficult to measure.
4. What is an acceptable range for the filter face velocity? A high velocity of sample gas may draw particulate (such as VOCs) through the filters or break down the filter material. A velocity that is low may not produce enough filter loading.
5. What type of filter medium is acceptable? Are there differences with non-diesel particulate which would dictate using a different type of filter material?
6. Is isokinetic sampling necessary? Isokinetic sampling is operating the particulate sample system so that the gas velocity in the particulate sample probe is the same, within some tolerance, as the gas velocity in the CVS bulk stream at the probe location. If this type of sampling is necessary, what tolerance should be used on the agreement of the two gas velocities?
7. Is a dilution tunnel necessary? A dilution tunnel is accepted practice for diesel testing. Is it still necessary for non-diesel particulate testing?
8. Are there special requirements for the vehicle tailpipe-to-CVS connector? Is insulation and/or heating desirable?
9. The current procedure calls for summing the net weight of the primary and secondary filters only if the ratio of net weights is less than 0.95. The ratio of net weights is the primary filter net weight divided by the sum of the primary and secondary filter net weights. We may consider summing the primary and secondary filter net weights regardless of the ratio. The secondary filter, if it collects anything, should be collecting particulate. Why should the secondary filter not be added to the total?

Alternatively, is a secondary filter necessary? Are there data that show the primary filter always collects the majority (like 99% or more) of the particulate matter? If so, perhaps the secondary filter is not necessary.

-3-

We began our own study of these questions last month. We will be examining these issues as expeditiously as possible in the coming months; some subsequent proposals to change the test procedure regulations may prove desirable.

Attachment

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# Slave Engine/Dynamometer Catalyst Studies at SWRI

## Summary

This study evaluates pollutant conversion efficiencies of catalysts from waiver fleet cars on a "slave engine - dynamometer" test apparatus under carefully controlled conditions. The conversion efficiency of catalysts from 11 HiTEC 3000 cars was compared with catalysts from 11 clear cars using a common source of inlet gas supply by all catalysts. This comparison provides a measure of HiTEC 3000 effect on catalyst activity isolated, insofar as possible, from external variability.

Based on these comparisons, there were no practical differences between clear and HiTEC 3000 catalysts removed from 5 models of the waiver test fleet after 75,000 accumulated miles of usage. In the single model which showed an effect, the HiTEC 3000 catalyst gave higher conversion efficiency than clear catalysts. Slave engine testing therefore demonstrates that HiTEC 3000 does not adversely affect operation of catalytic converters.

## Description of Test Protocol

A carefully controlled and regulated "slave engine-dynamometer" apparatus provided a common source of inlet gas to all study catalysts by utilizing a 350 in<sup>3</sup> Chevrolet V-8 test engine. Catalysts were removed from the following fleet cars for study:

<u>Car</u>	<u>Number of Monoliths</u>
Ford Escort 1.9 L	6
Ford Taurus 3.0 L	6
GM Buick Century 2.8 L	6
GM Buick Century 3.8 L	2
Ford Crown Victoria 5.0 L	<u>4</u> (from 2 cars)
Total	24

The catalysts were matched with respect to clear and HiTEC 3000 usage (equal numbers of clear and HiTEC 3000 catalysts were used).

The recorded inlet and outlet gas compositions are averaged<sup>1/</sup> and used to calculate conversion efficiency as below:

$$\text{Conversion} = \left( 1 - \frac{\text{Outlet Concentration}}{\text{Inlet Concentration}} \right) \times 100$$

This computation is performed for the three regulated pollutants at seven air/fuel ratios for each catalyst evaluated.

<sup>1/</sup>Since the air/fuel ratio is modulated at a frequency of 1 Hz for all tests, the instantaneous values for gas composition vary with time about the mean (nominal) air/fuel ratio.

A widely used descriptive measure of catalyst gas inlet composition is the redox ratio relating the reducing to oxidizing components. This value is calculated from catalyst inlet composition as below:

$$\text{Redox Ratio} = \frac{1.33^{2/} \times [\text{CO}] + [\text{C}]}{[\text{NOX}] + 2 [\text{O}_2]}$$

where  $[\text{CO}]$  = carbon monoxide concentration

$[\text{C}]$  = carbon concentration from hydrocarbons

$[\text{NOX}]$  = nitrogen oxide concentration

$[\text{O}_2]$  = oxygen concentration

Conversion efficiency for a given redox ratio should be comparable between catalysts. Redox ratio is an attribute of combustion gases that indicates how far the composition is from a stoichiometric mixture.<sup>3/</sup> For redox ratios  $\leq 1$ , the catalyst can convert all oxidizable components to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , but for redox ratios  $> 1.0$  complete conversion cannot be attained. A graphical comparison between catalysts gives a good visual picture of the relationship between efficiency and redox ratio. However, this method is time consuming and no statistical confidence statements can be made about the visual comparisons. Mathematical models were used to relate conversion efficiency with redox ratio. These models were developed by regression analysis of the data.

Conversion efficiency for each pollutant was regressed to obtain a "best fit" relationship with redox ratio for each car model studied. These "best fit" relationships were used for within car model comparisons between catalysts from cars that used clear and HiTEC 3000 fuels.

<sup>2/</sup> The 1.33 multiplier for  $[\text{CO}]$  accounts for the average concentration of hydrogen in exhaust gas.

<sup>3/</sup> Redox ratios less than 1.0 indicate excess air (lean) and greater than 1.0 indicate excess fuel (rich) condition and a redox ratio of 1.0 represents a stoichiometric mixture.

A more powerful test for significant differences is an examination of confidence intervals about the "best fit" curves for clear and HiTEC 3000 conversion efficiencies. The comparison of interest is the difference between the upper 95% confidence limits of the HiTEC 3000 curve and the lower 95% confidence limits of the clear curve. Their coincidence shows that when the variability of the data is considered there is no significant difference between clear and HiTEC 3000 catalysts.

#### GM Buick 3.8 l Carbon Monoxide Conversion

Again, a comparison of the upper 95% confidence limits of the HiTEC 3000 curve includes the lower 95% confidence limits for the clear curve and therefore there is no significant difference between clear and HiTEC 3000 catalysts. Further, there being only one clear and one HiTEC 3000 catalyst, it is not possible to decide if any differences are attributable to HiTEC 3000 or to catalyst-to-catalyst variation.<sup>6/</sup>

#### Ford Crown Victoria 5.0 l All Pollutants

The differences noted for HC, CO, and NOX in the above tabulation are significantly different for clear and HiTEC 3000 catalysts. There is no coincidence of the confidence limits for the hydrocarbon, carbon monoxide or nitrogen oxide conversion efficiency relationships for clear and HiTEC 3000 catalyst. Hence, one concludes that a significant overall difference exists for these catalysts; i.e. the conversion efficiencies for all pollutants is higher for HiTEC 3000.<sup>7/</sup>

However, with only two cars available for evaluation, the effect may be a catalyst-to-catalyst variation as opposed to a HiTEC 3000 effect. This is very plausible when one recalls that the Crown Victoria cars showed great variability in emissions throughout the fleet tests. These differences may exist, but attributing the differences to HiTEC 3000 is speculative.

#### Conclusion

The results of this study are depicted graphically by conversion efficiency plots showing the actual data points, best fit line and upper and lower 95% confidence limits for each pollutant and car. These graphs are shown in Figures 1 through 30 of Attachment 1.

Of the 5 car models tested, only one car model showed significant overall differences between clear and HiTEC 3000 catalysts. In this instance, the HiTEC 3000 catalysts showed greater conversion efficiency than clear catalysts. Slave engine testing therefore demonstrates that HiTEC 3000 does not adversely affect operation of catalytic converters.

<sup>6/</sup>The graphs of this result are shown in Figure 9 and 10 in Attachment 1.

<sup>7/</sup>The graphs of these results are shown in Figure 25-Figure 30 of Attachment 1.

The following tabulation lists the significant overall differences found:

Differences in Overall Catalyst  
Conversion Efficiency  
(HiTEC 3000 - Clear)\*

Car I.D.	Pollutant		
	HC	CO	NOX
GM Buick 2.8 l	- 2.73 (88.2) <sup>4/</sup>	N.S.	N.S.
GM Buick 3.8l	N.S.	- 3.97 (91.9)	N.S.
Ford Crown Victoria	+ 13.1 (70.6)	+ 17.38 (62.5)	+ 8.91 (54.1)
Ford Escort 1.9 l	N.S.	N.S.	N.S.
Ford Taurus 3.0 l	N.S.	N.S.	N.S.

\* A positive value indicates that HiTEC 3000 had a higher conversion efficiency than clear fuel.

Where N.S. = Not Significant.

The average differences above are determined from regression analysis. Each difference will be discussed individually.

GM Buick 2.8 l Hydrocarbon Conversion

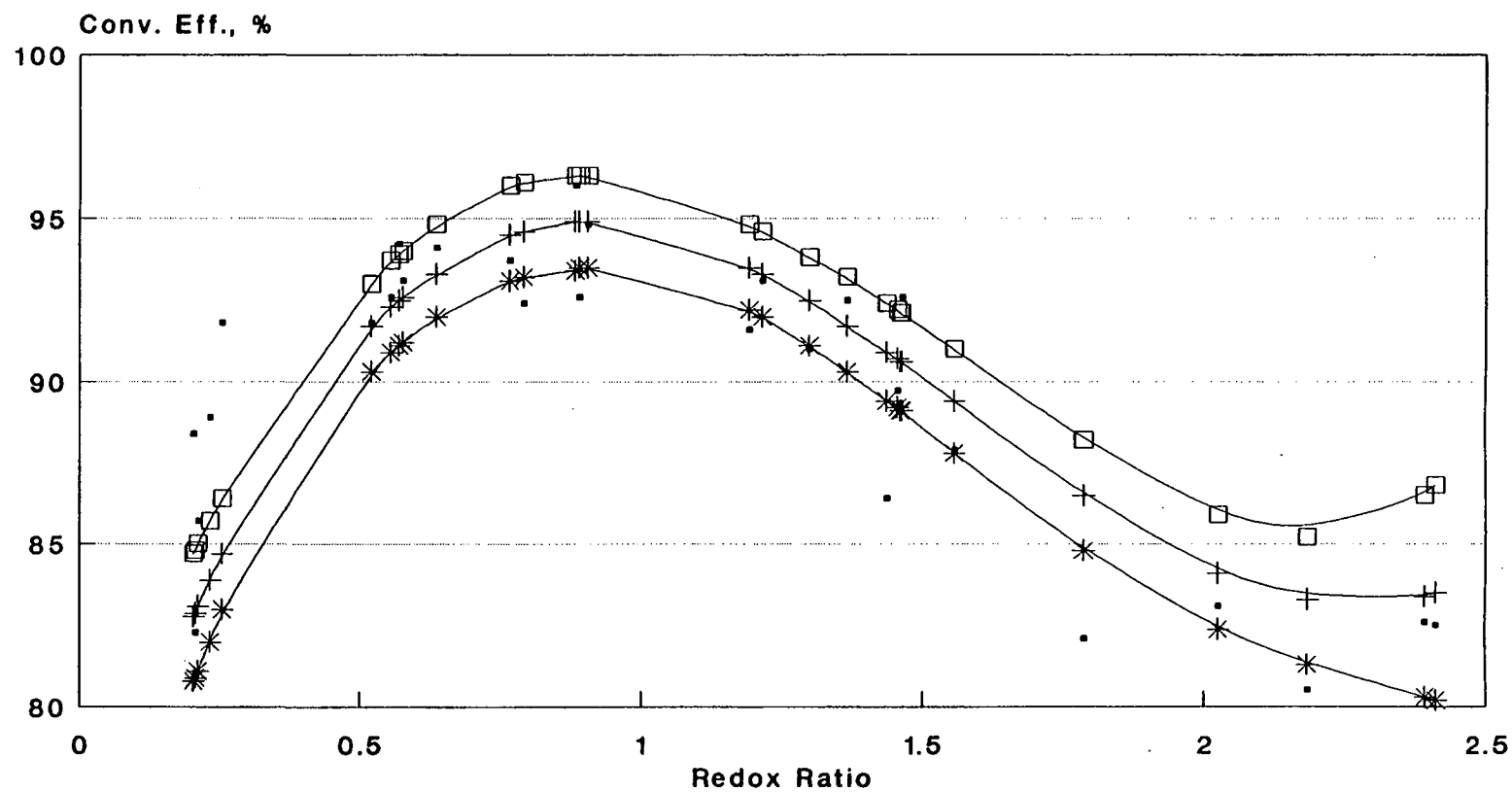
Figures 1 and 2 are plots<sup>5/</sup> of hydrocarbon conversion efficiency vs. redox ratio for the 2.8 l Buicks. The hydrocarbon conversion efficiencies for redox ratios greater than about 0.6 do not appear to show any difference between clear and HiTEC 3000 from inspection. The <0.6 redox ratio conversion efficiency data are highly variable (duplicate runs for the same cars and fuel varied by as much as 9 percent for redox values in the range of 0.2-0.25). This variability is strikingly evident from Figure 1 for the lowest redox ratios. This large variability is partly due to analytical problems with measuring hydrocarbons at the low levels encountered at these redox ratios (very lean mixture). Engine-out hydrocarbons for redox ratios of 0.2-0.25 were in the range of 60 ppm and tailpipe emissions were about 6 ppm. At these low levels, an error of 3 ppm causes a conversion efficiency change of about 10 percent (85%-95%). This problem was more evident for the 2.8 l Buicks because hydrocarbons emissions were lower (by a factor of about 50%) than for any other catalyst tested. Examination of Figures 1 and 2 shows that seven observations at the lowest redox ratios are the probable cause of the significant overall difference between clear and HiTEC 3000 catalyst efficiencies. These points involve three observations for clear cars and four observations for HiTEC 3000 cars. When values below a redox ratio of 0.6 are omitted, an identical regression analysis shows that the difference is non-significant (results are not reported herein).

<sup>4/</sup> The numbers in parenthesis are the average conversion efficiencies for all catalyst (clear and HiTEC 3000).

<sup>5/</sup> These graphs are shown in Attachment 1.

## Attachments

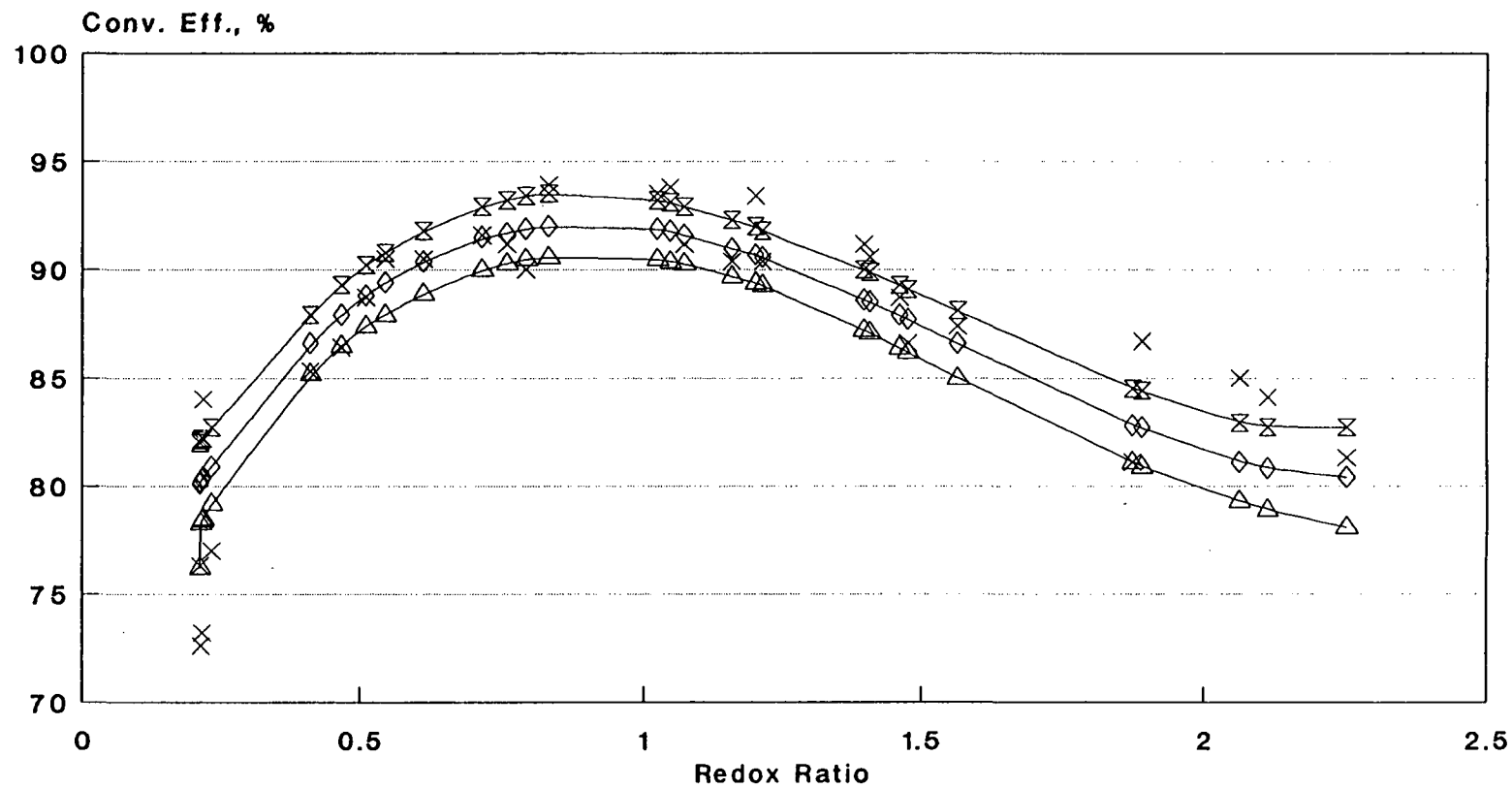
Figure 1  
Hydrocarbon Conversion Eff., Percent  
Buick Century 2.8 l



• Data Points + Best Fit Line \* Lower 95% C.L. □ Upper 95% C.L.

Data for Car No.'s 1,2,5 → Clear

**Figure 2**  
**Hydrocarbon Conversion Eff., Percent**  
**Buick Century 2.8 I**

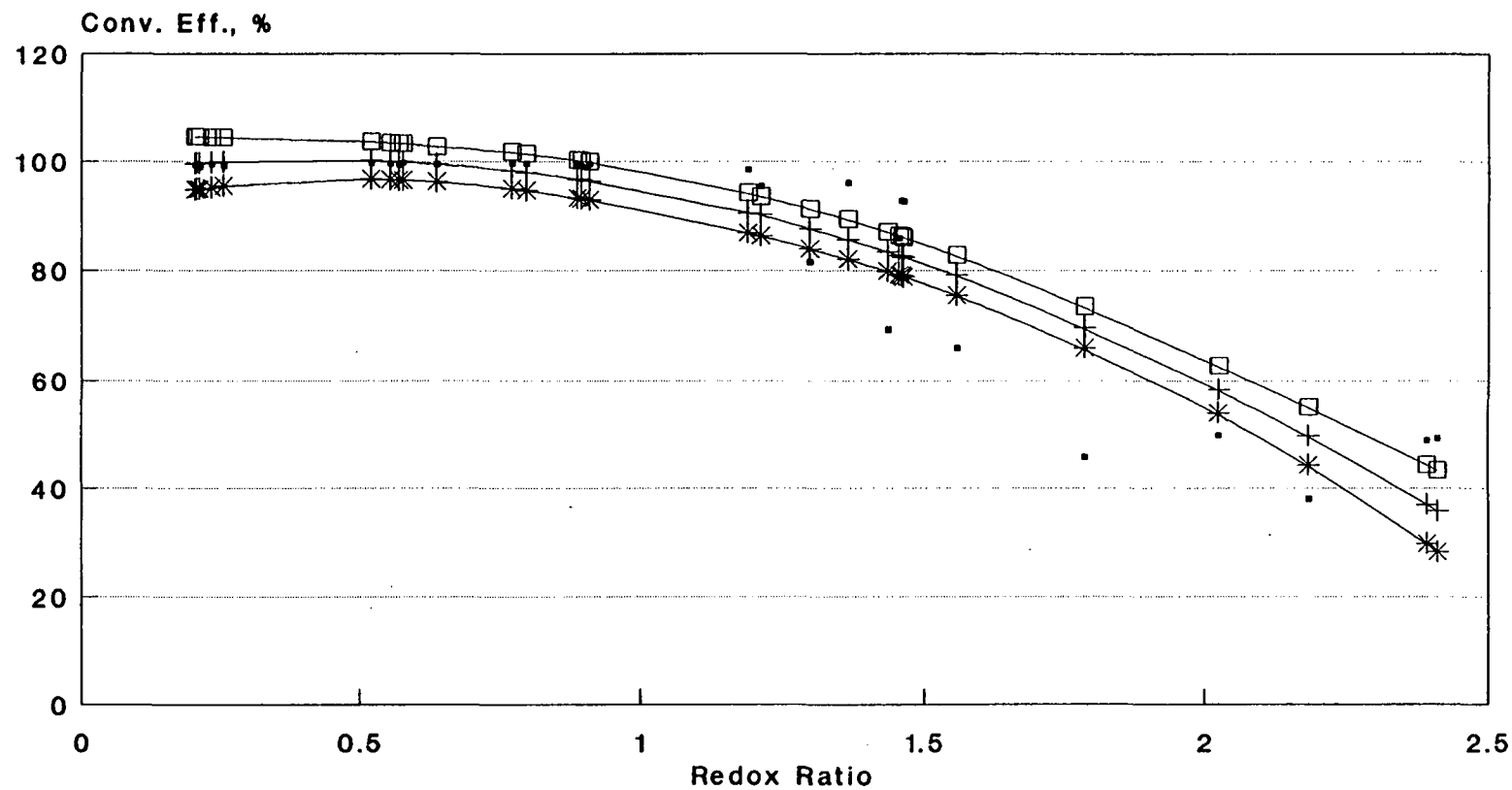


**HiTEC 3000 FUEL**

X Data Points    ◇ Best Fit Line    △ Lower 95% C.L.    ✕ Upper 95% C.L.

Data for Car No.'s 3,4,6 → HiTEC 3000

Carbon Monoxide Conversion Eff., Percent  
Buick Century 2.8 I



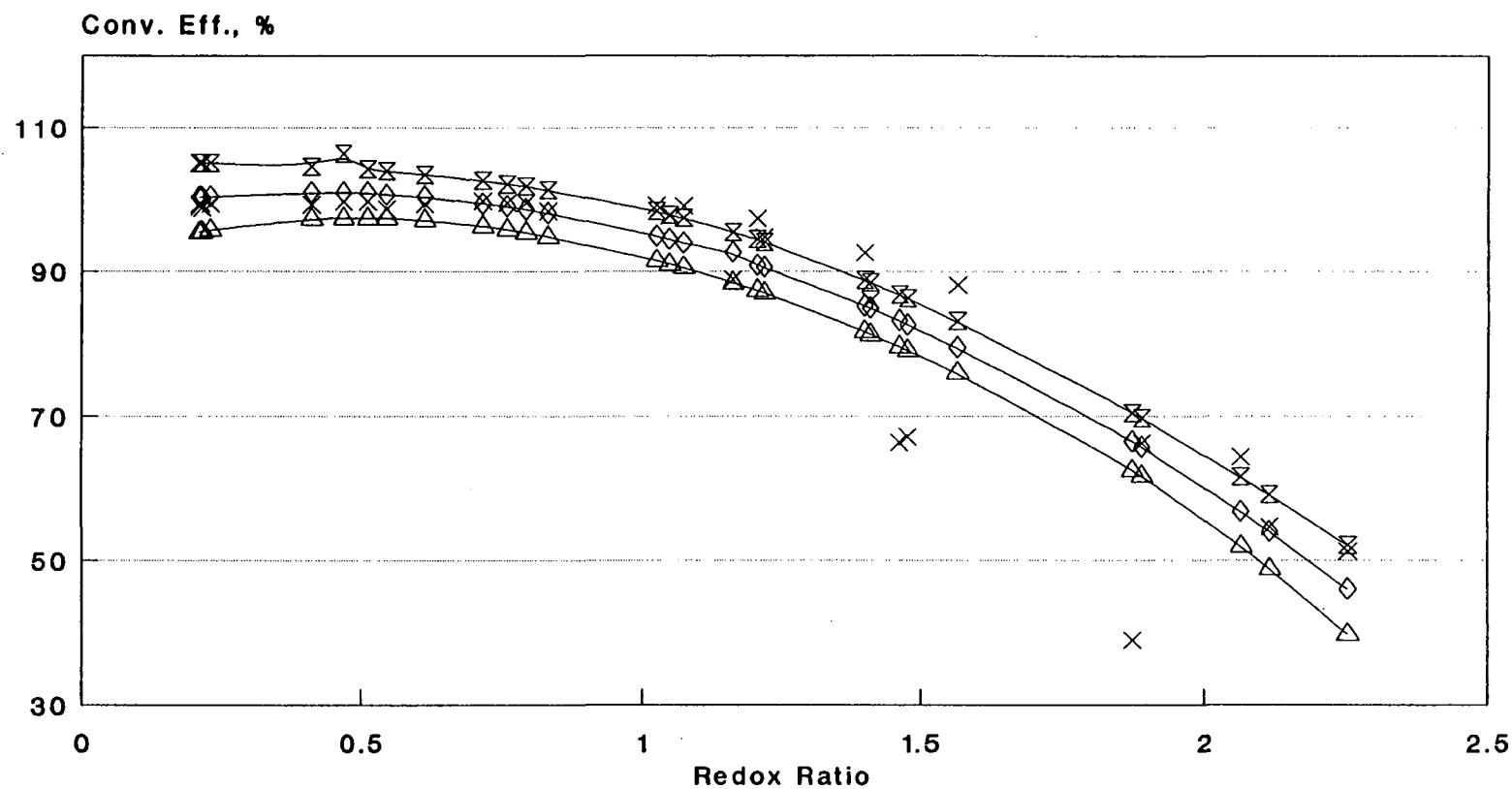
## CLEAR FUEL

• Data Points    + Best Fit Line    \* Lower 95% C.L.    □ Upper 95% C.L.

**Data for Car No.'s 1,2,5 -> Clear**



**Figure 4**  
Carbon Monoxide Conversion Eff., Percent  
Buick Century 2.8 I

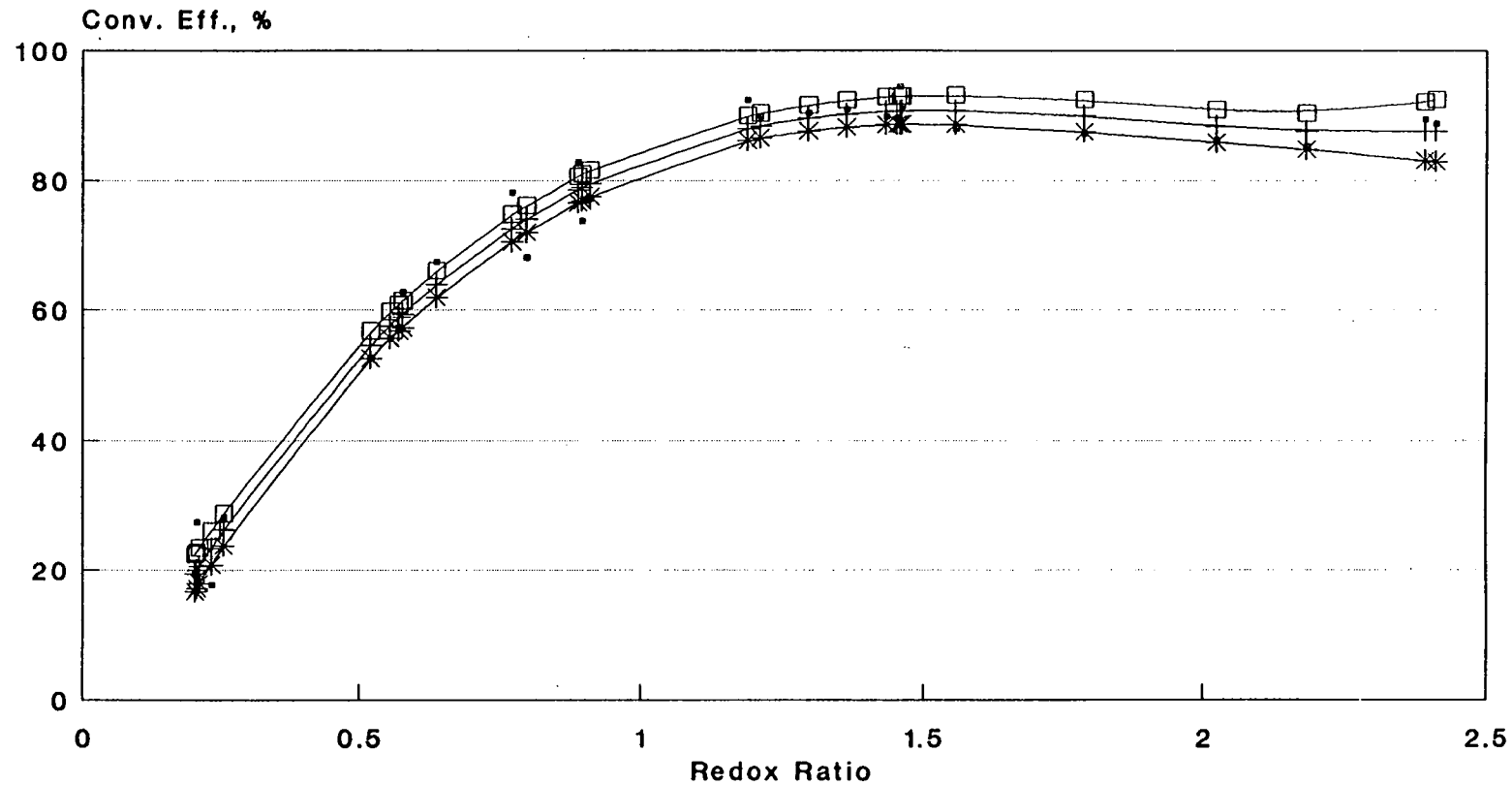


**HiTEC 3000 FUEL**

× Data Points    ◇ Best Fit Line    △ Lower 95% C.L.    ✕ Upper 95% C.L.

Data for Car No.'s 3,4,6 → HiTEC 3000

Figure 5  
Nitrogen Oxide Conversion Eff., Percent  
Buick Century 2.8 l

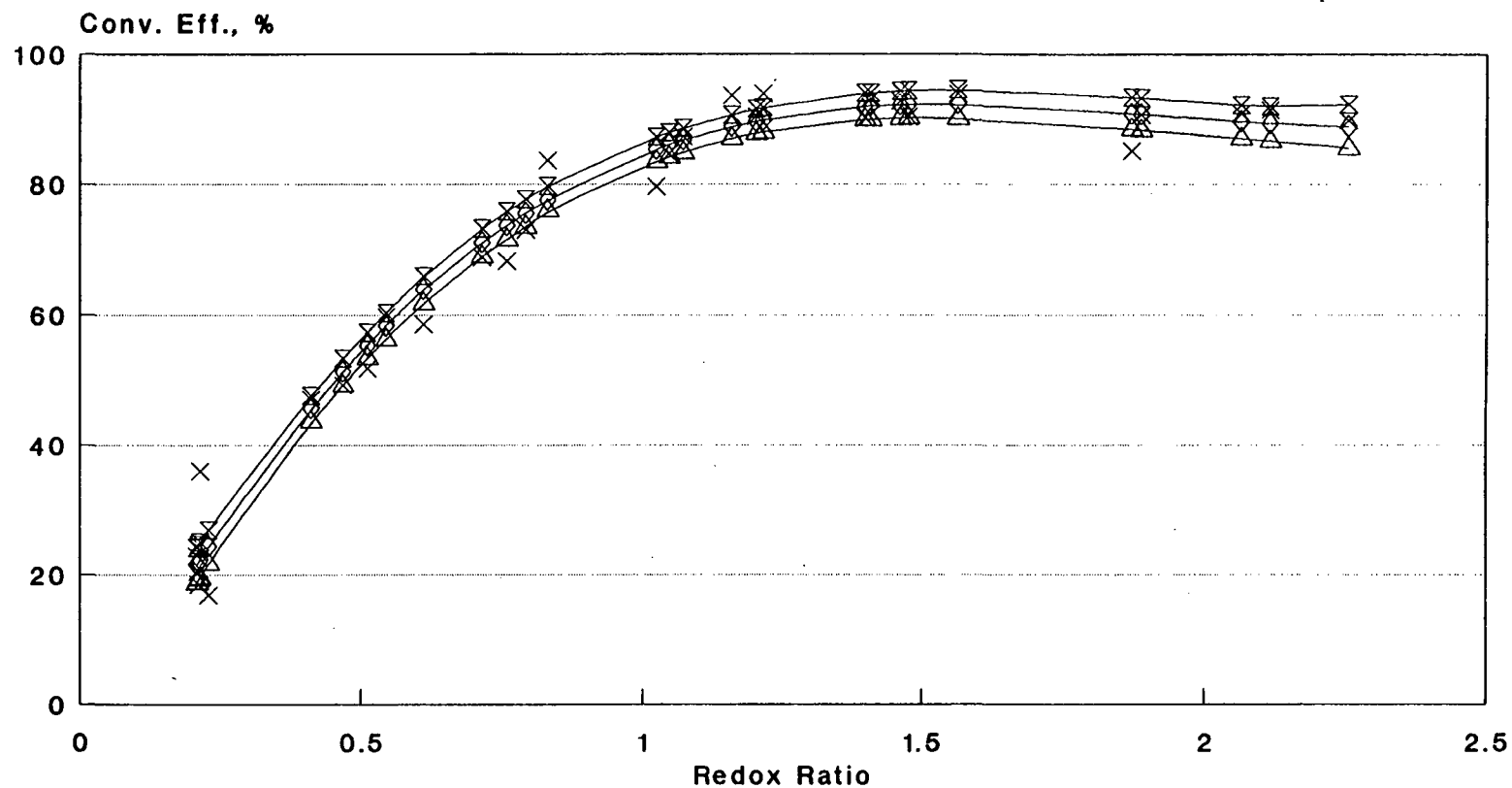


**CLEAR FUEL**

• Data Points    + Best Fit Line    \* Lower 95% C.L.    □ Upper 95% C.L.

Data for Car No.'s 1,2,5 → Clear

**Figure 6**  
**Nitrogen Oxide Conversion Eff., Percent**  
**Buick Century 2.8 I**

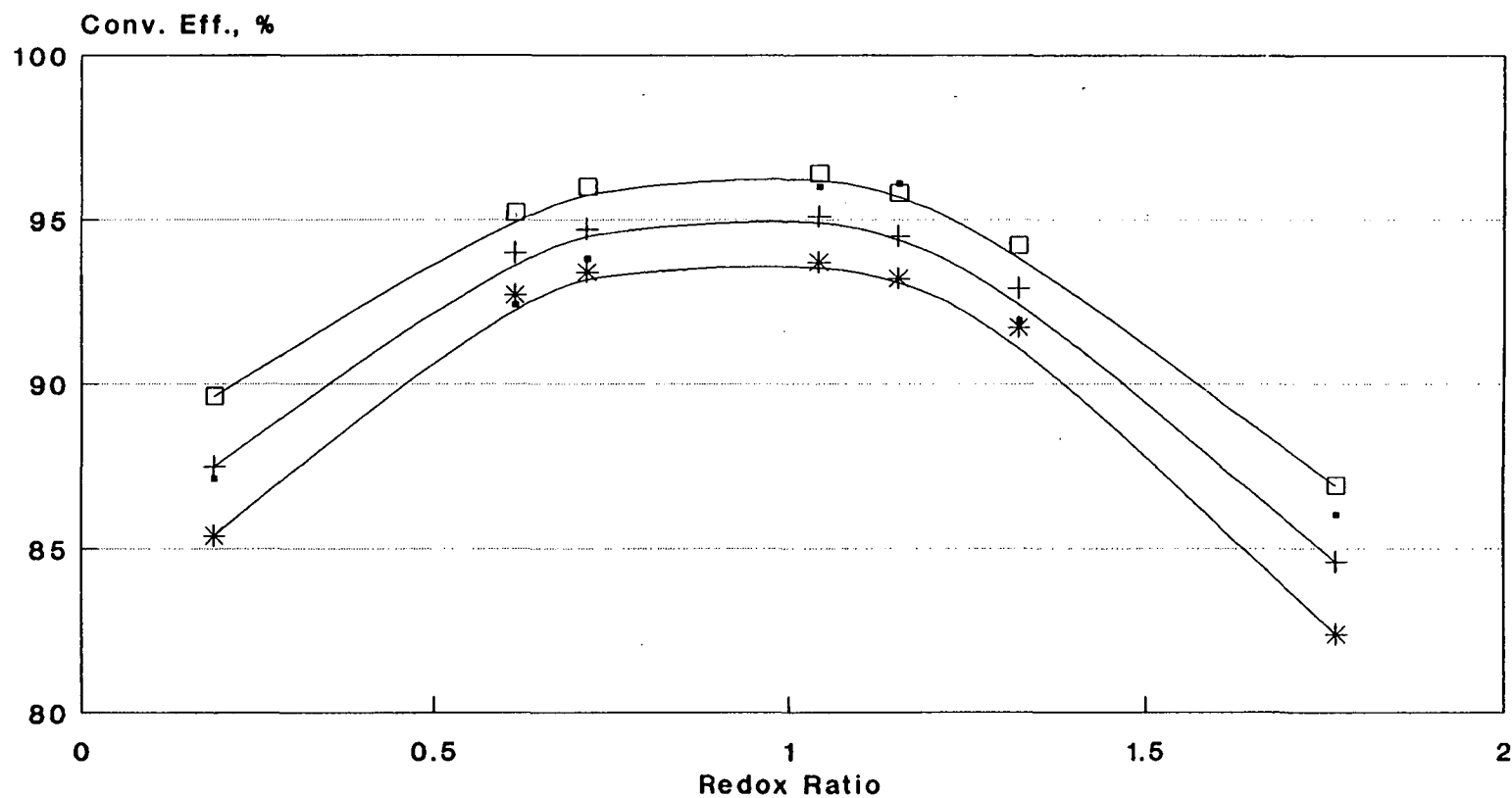


**HITEC 3000 FUEL**

× Data Points    ◇ Best Fit Line    △ Lower 95% C.L.    ⊠ Upper 95% C.L.

Data for Car No.'s 3,4,6 → HITEC 3000

Figure 7  
Hydrocarbon Conversion Eff., Percent  
Buick Century 3.8 l

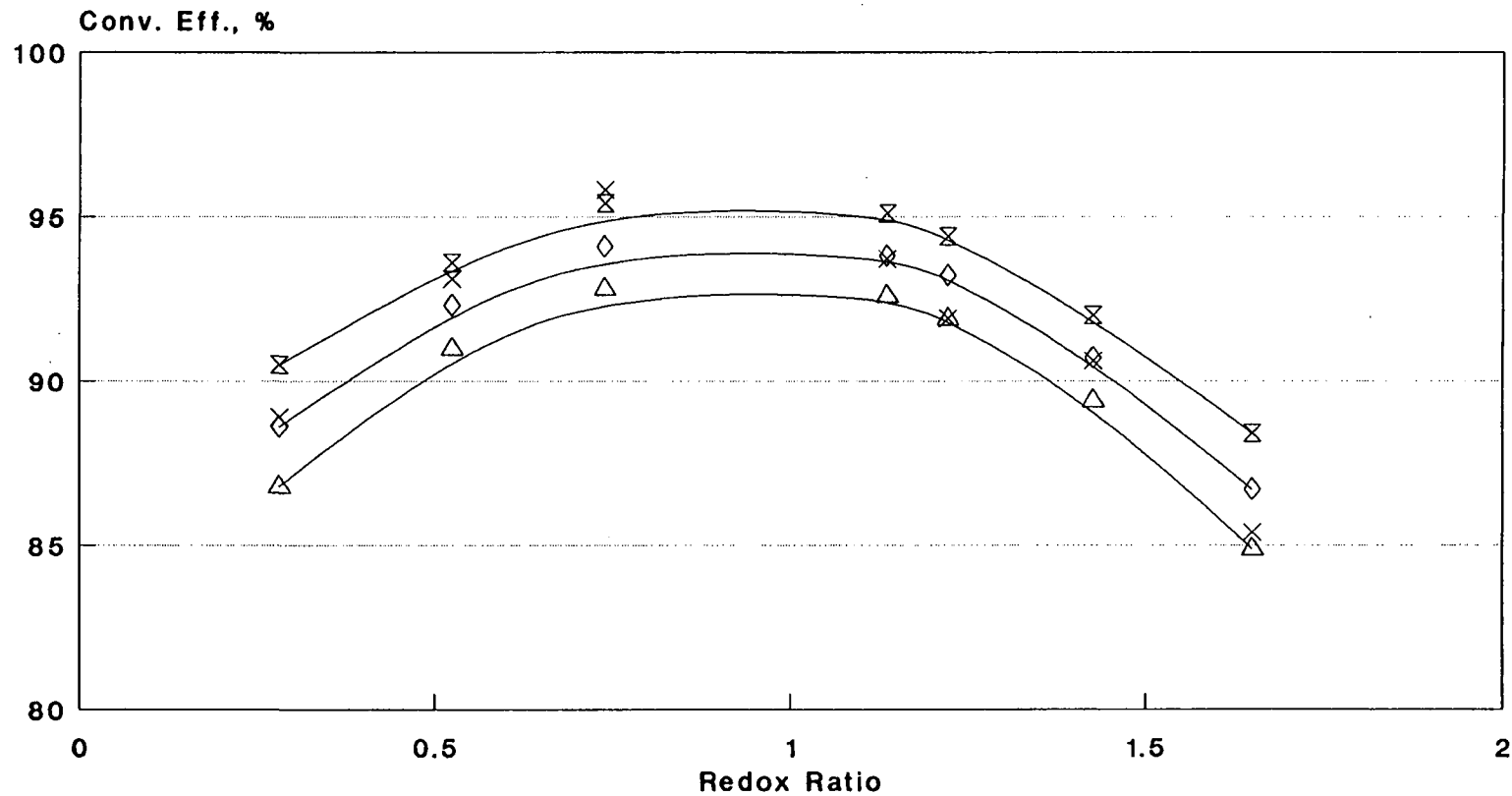


CLEAR FUEL

• Data Points    + Best Fit Line    \* Lower 95% C.L.    □ Upper 95% C.L.

Data for Car No.'s 3 → Clear

Figure 8  
Hydrocarbon Conversion Eff., Percent  
Buick Century 3.8 I

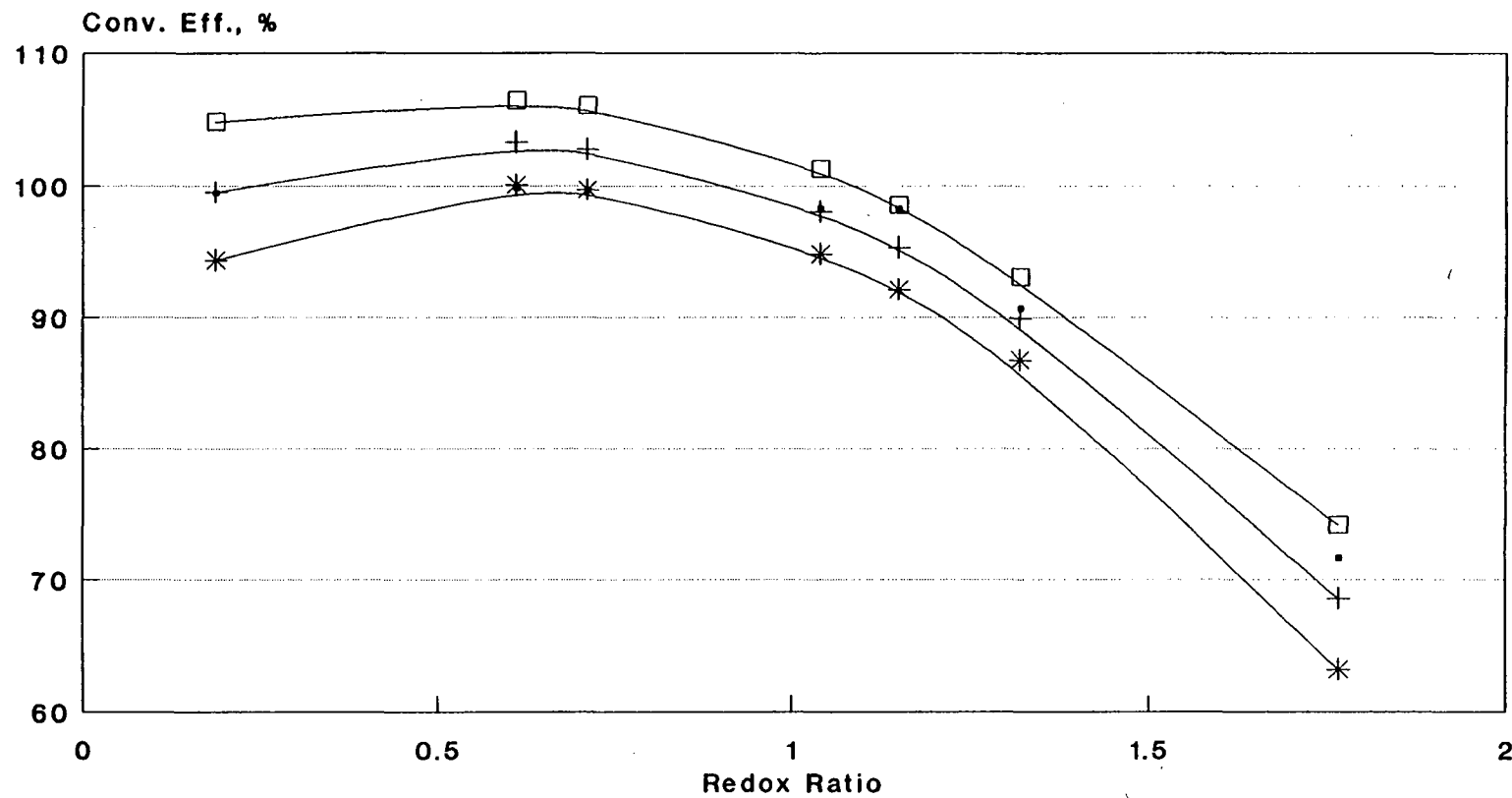


HiTEC 3000 FUEL

× Data Points    ◇ Best Fit Line    △ Lower 95% C.L.    × Upper 95% C.L.

Data for Car No.'s 4 → HiTEC 3000

**Figure 9**  
Carbon Monoxide Conversion Eff., Percent  
Buick Century 3.8 l

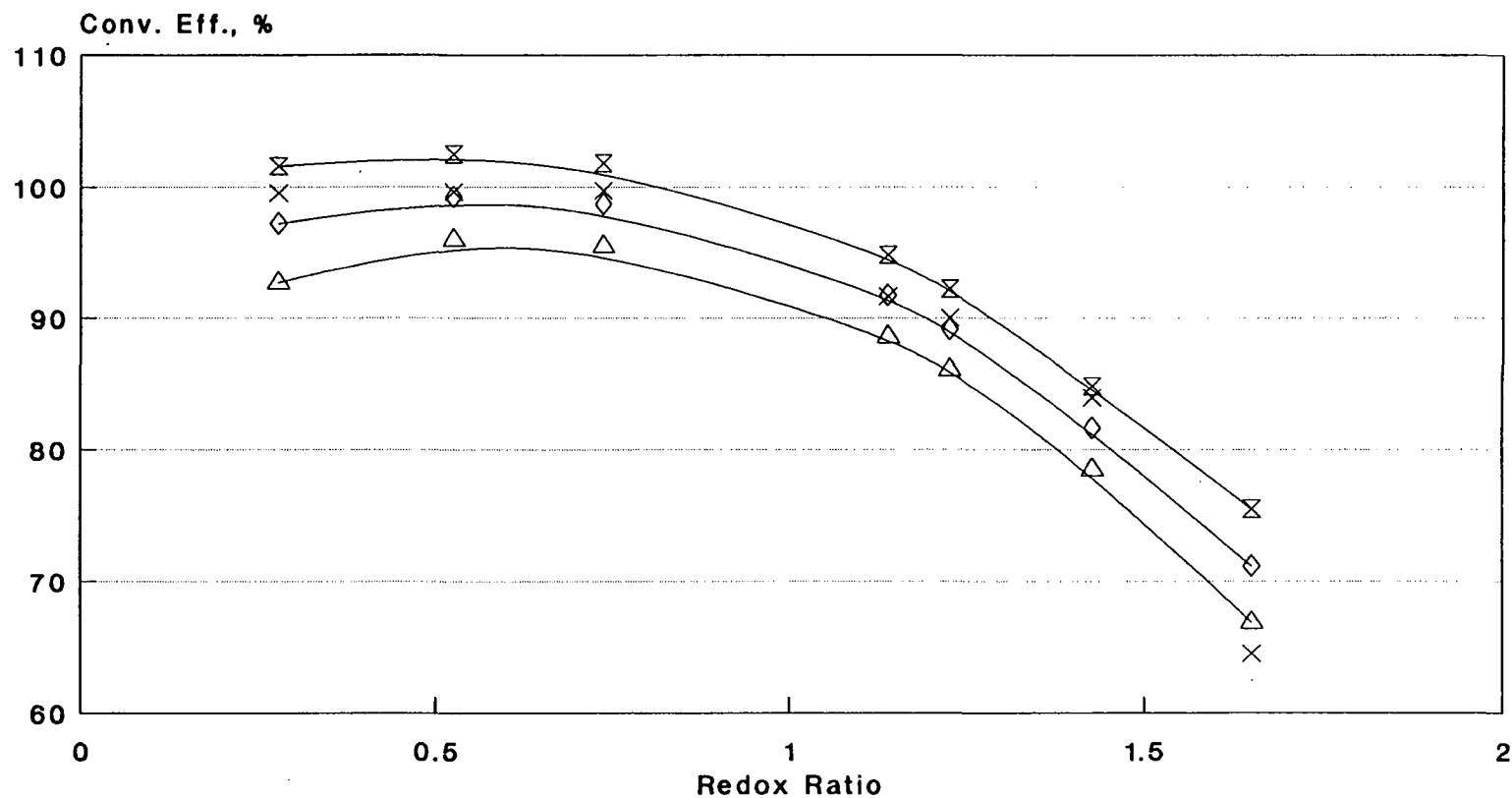


**CLEAR FUEL**

■ Data Points    + Best Fit Line    \* Lower 95% C.L.    □ Upper 95% C.L.

Data for Car No.'s 3 → Clear

**Figure 10**  
Carbon Monoxide Conversion Eff., Percent  
Buick Century 3.8 l

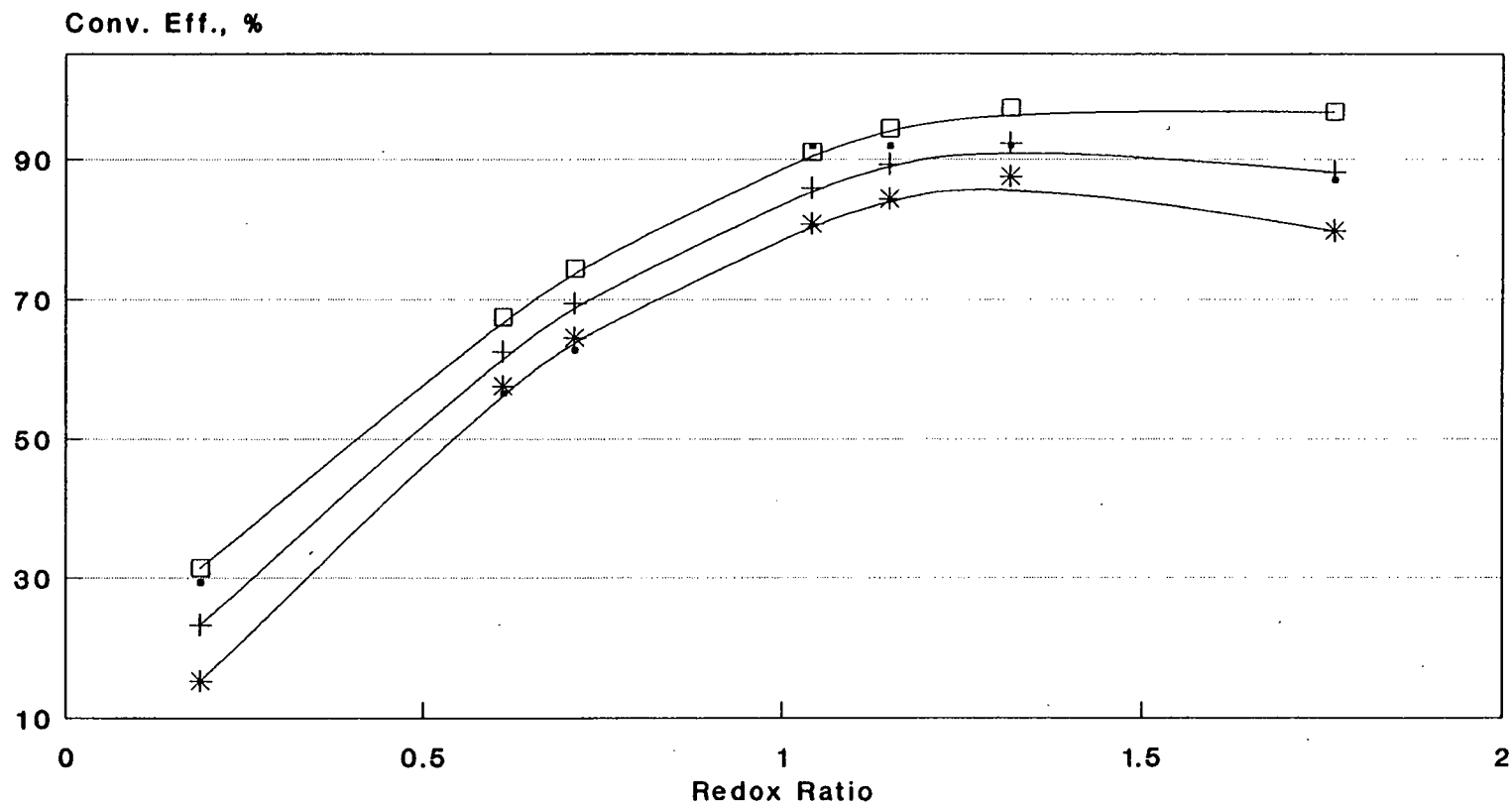


**HiTEC 3000 FUEL**

× Data Points    ◇ Best Fit Line    △ Lower 95% C.L.    ✕ Upper 95% C.L.

Data for Car No.'s 4 → HiTEC 3000

Figure 11  
Nitrogen Oxide Conversion Eff., Percent  
Buick Century 3.8 l



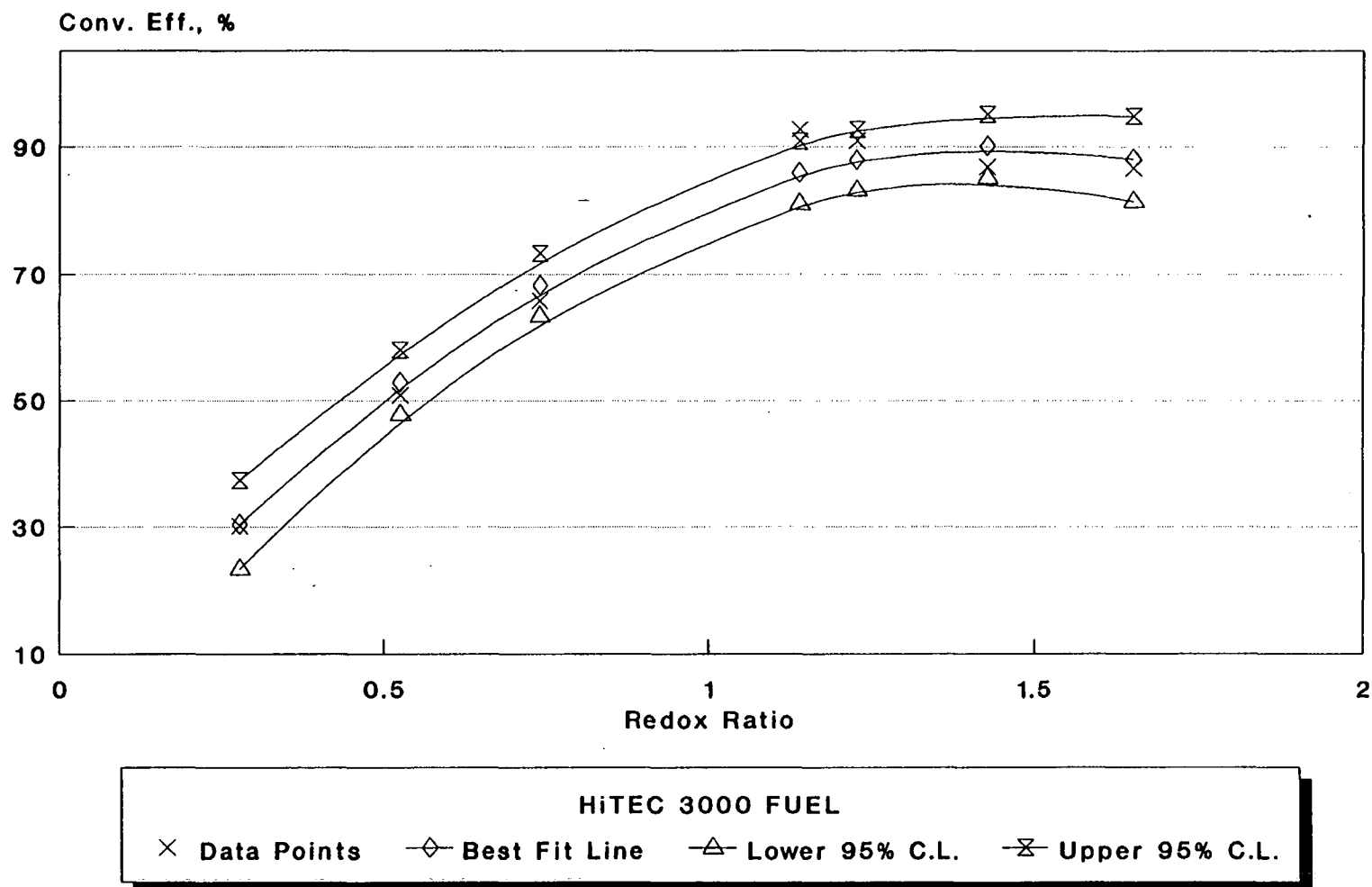
CLEAR FUEL

• Data Points    + Best Fit Line    \* Lower 95% C.L.    □ Upper 95% C.L.

Data for Car No.'s 3 → Clear

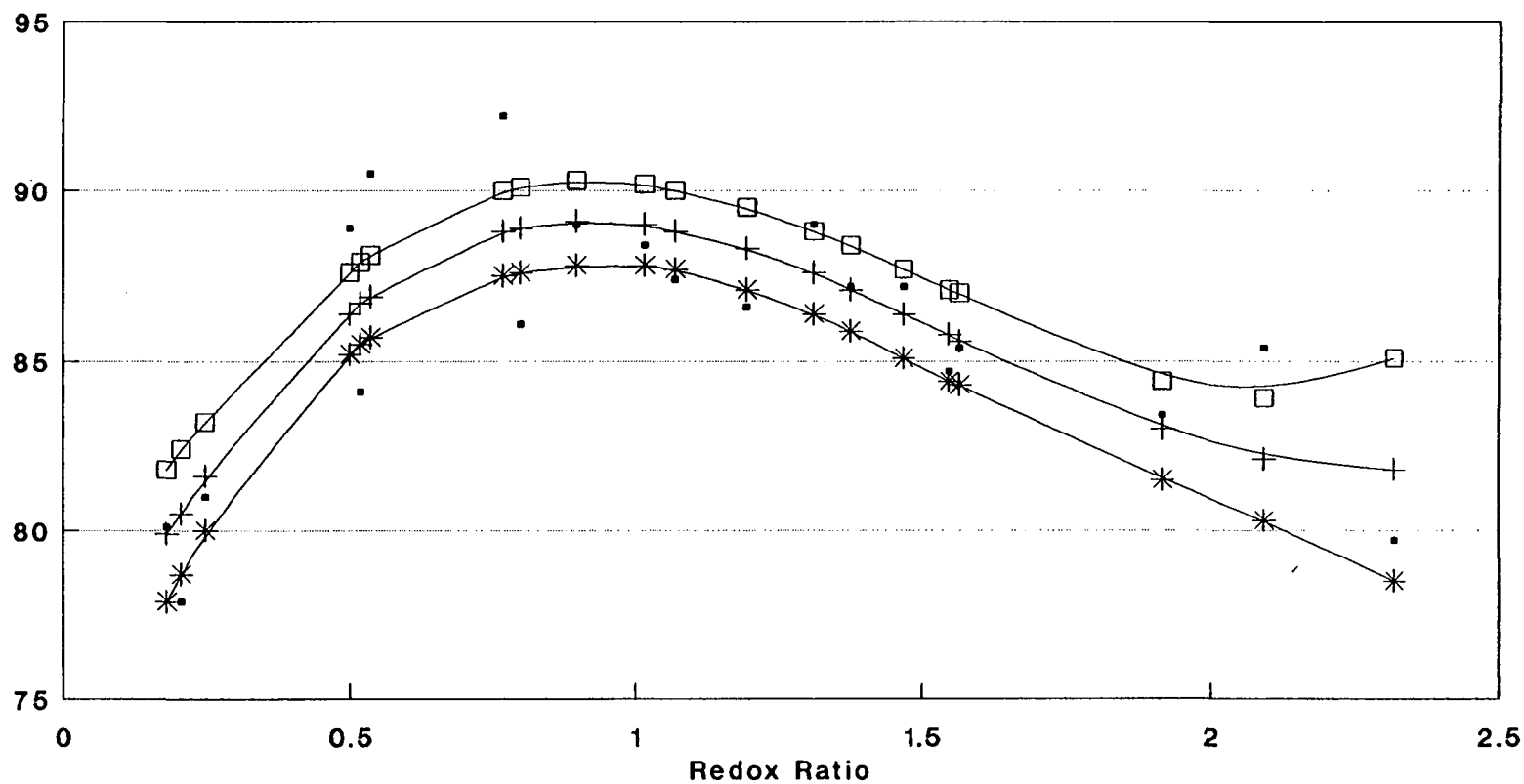


**Figure 12**  
**Nitrogen Oxide Conversion Eff., Percent**  
**Buick Century 3.8 I**



Data for Car No.'s 4 → HiTEC 3000

Figure 13  
Hydrocarbon Conversion Eff., Percent  
Ford Taurus 3.0 I

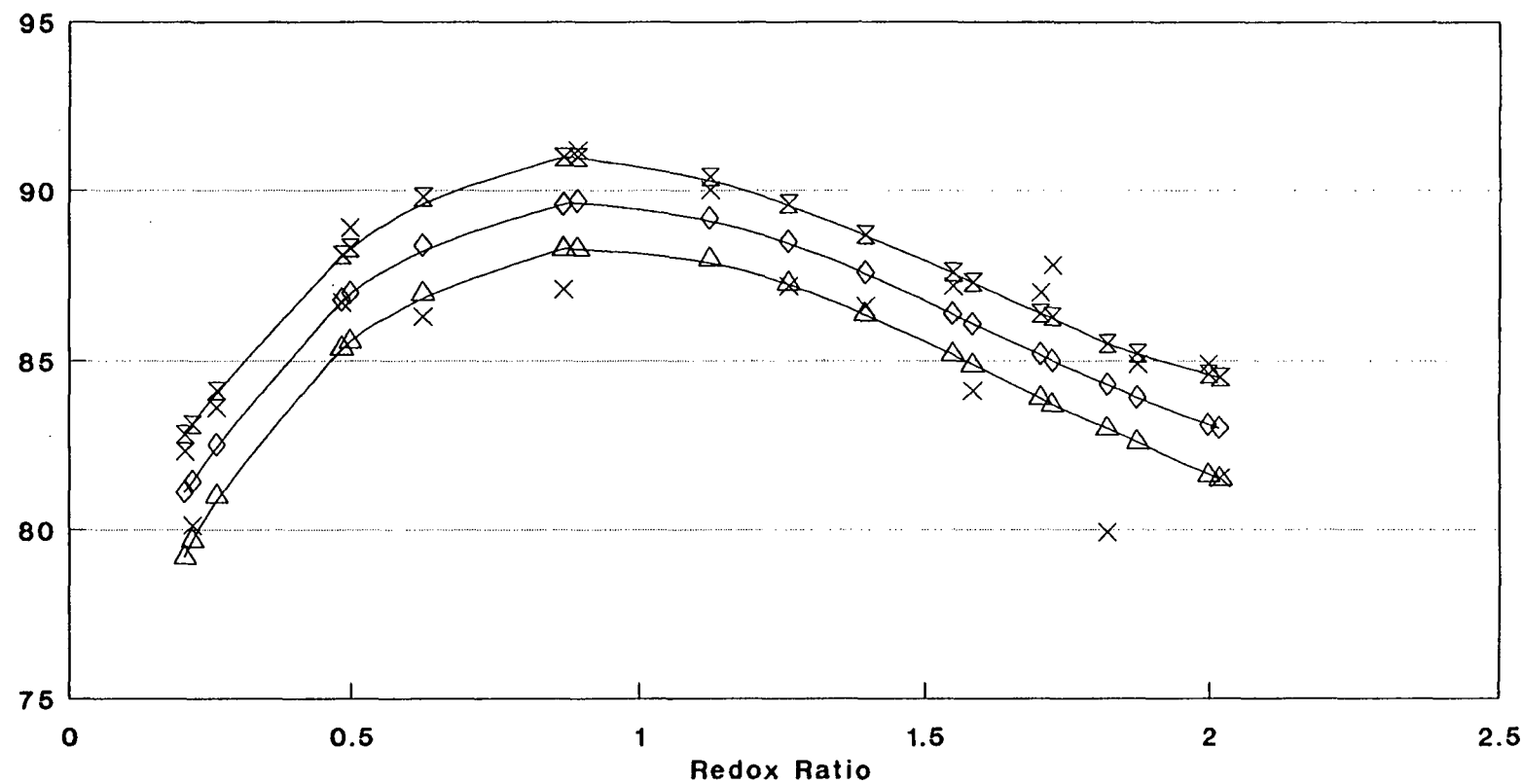


CLEAR FUEL

• Data Points    + Best Fit Line    \* Lower 95% C.L.    □ Upper 95% C.L.

Data for Car No.'s 2, 3, 5 → Clear

Figure 14  
Hydrocarbon Conversion Eff., Percent  
Ford Taurus 3.0 l

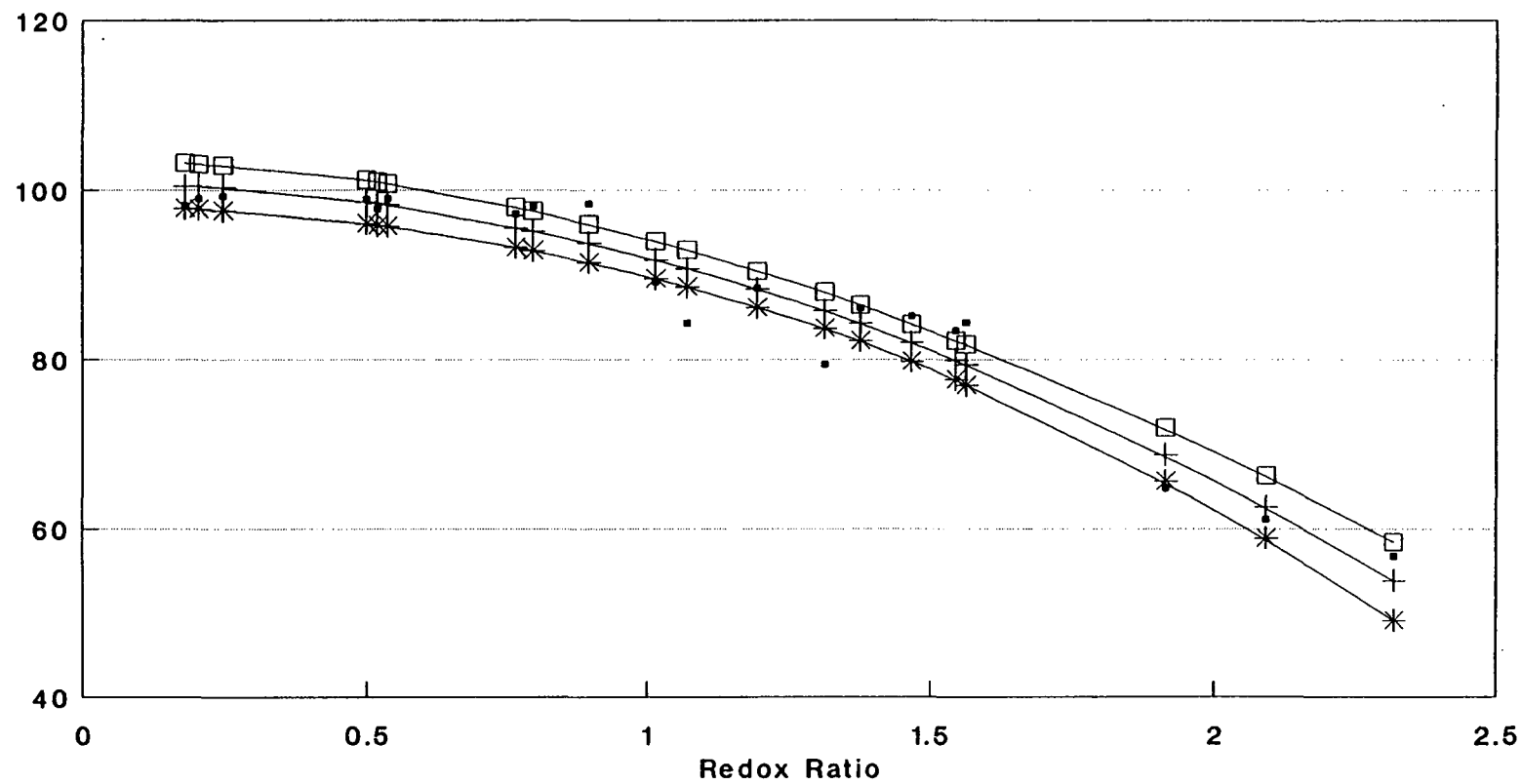


HiTEC 3000 FUEL

× Data Points    ◇ Best Fit Line    △ Lower 95% C.L.    x Upper 95% C.L.

Data for Car No.'s 1, 4, 6 → HiTEC 3000

**Figure 15**  
**Carbon Monoxide Conversion Eff., Percent**  
**Ford Taurus 3.0 I**

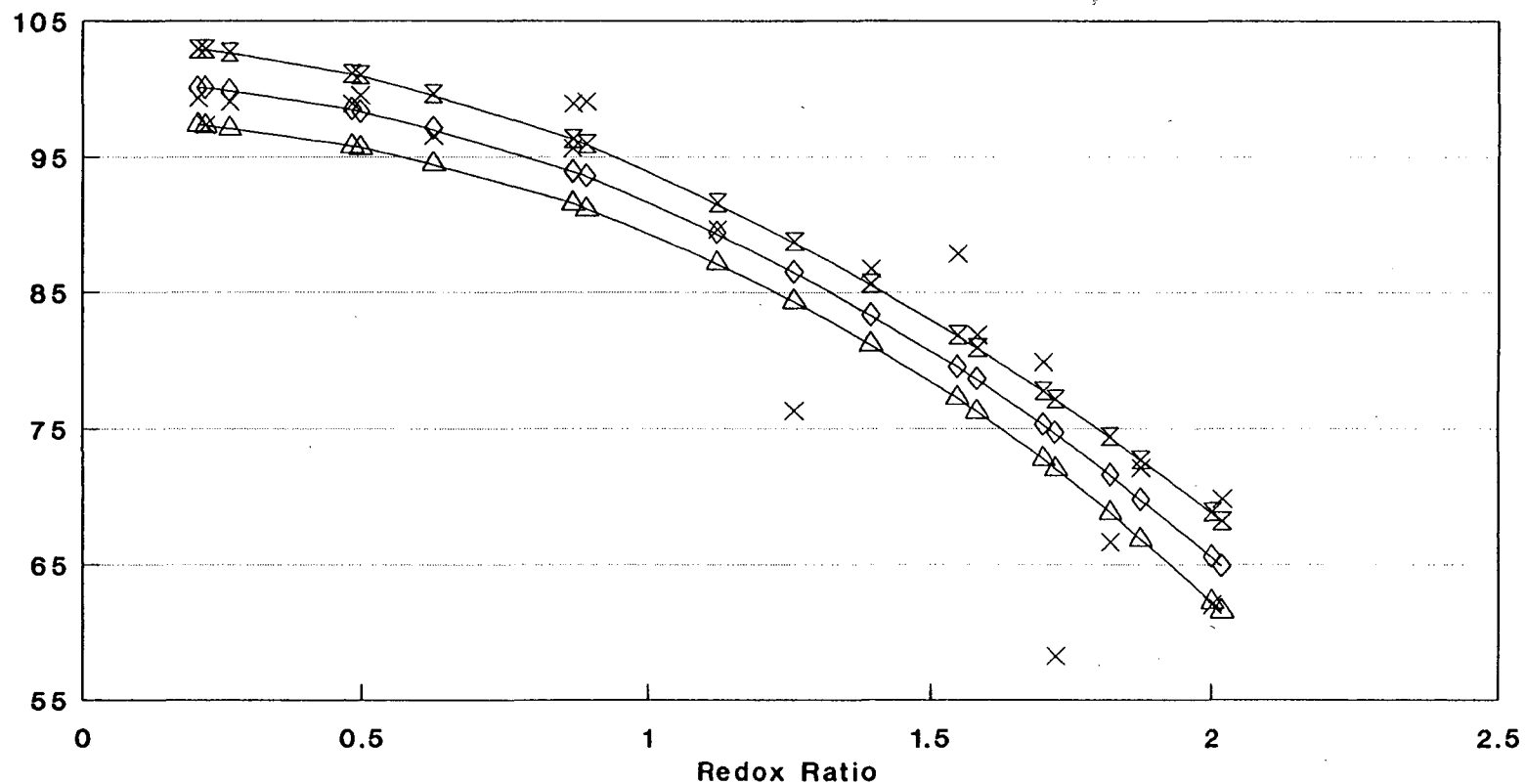


**CLEAR FUEL**

• Data Points    + Best Fit Line    \* Lower 95% C.L.    □ Upper 95% C.L.

Data for Car No.'s 2, 3, 5 → Clear

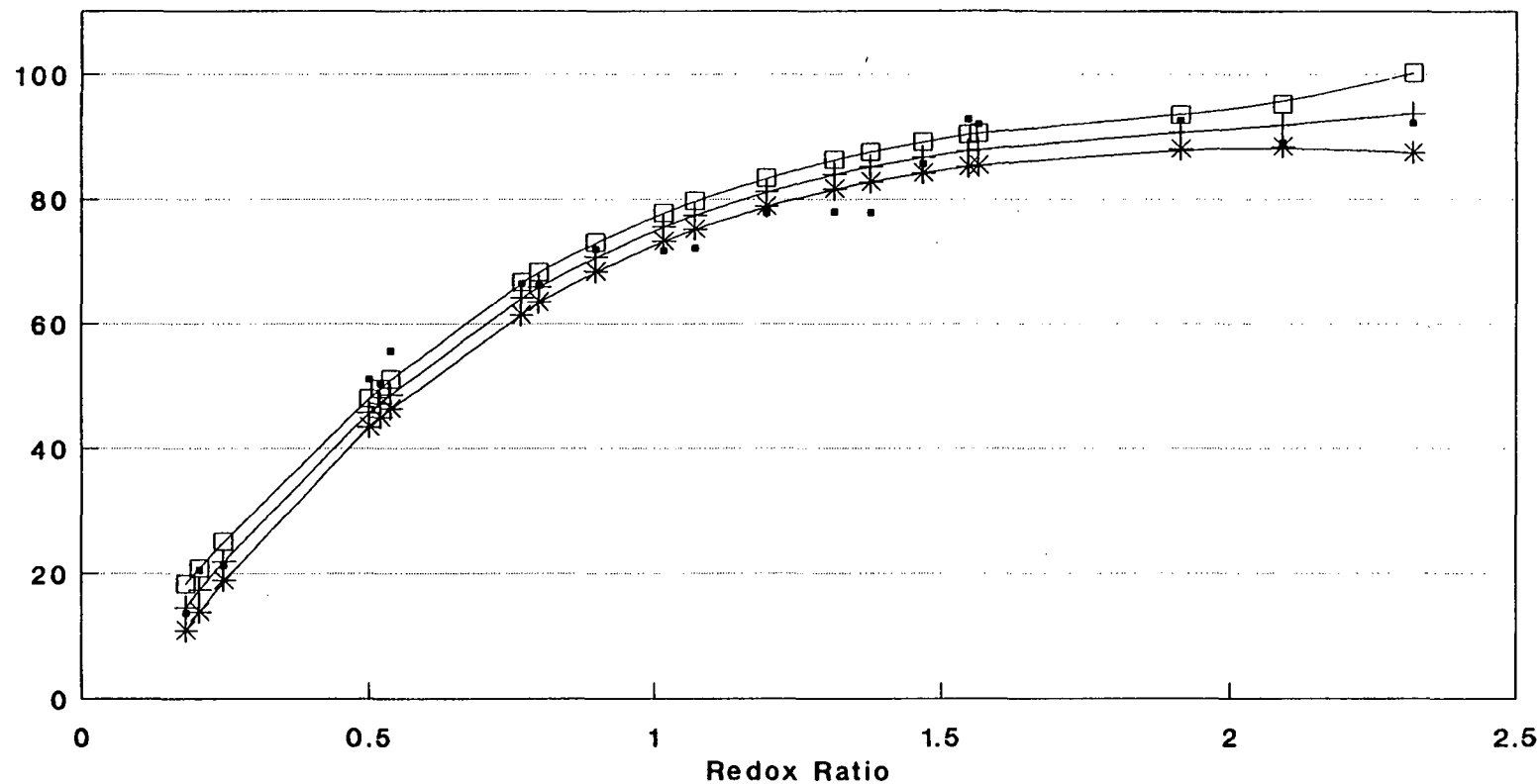
Figure 16  
Carbon Monoxide Conversion Eff., Percent  
Ford Taurus 3.0 I



HiTEC 3000 FUEL  
 x Data Points    ◇ Best Fit Line    △ Lower 95% C.L.    ⊠ Upper 95% C.L.

Data for Car No.'s 1, 4, 6 → HiTEC 3000

Figure 17  
 Nitrogen Oxide Conversion Eff., Percent  
 Ford Taurus 3.0 I

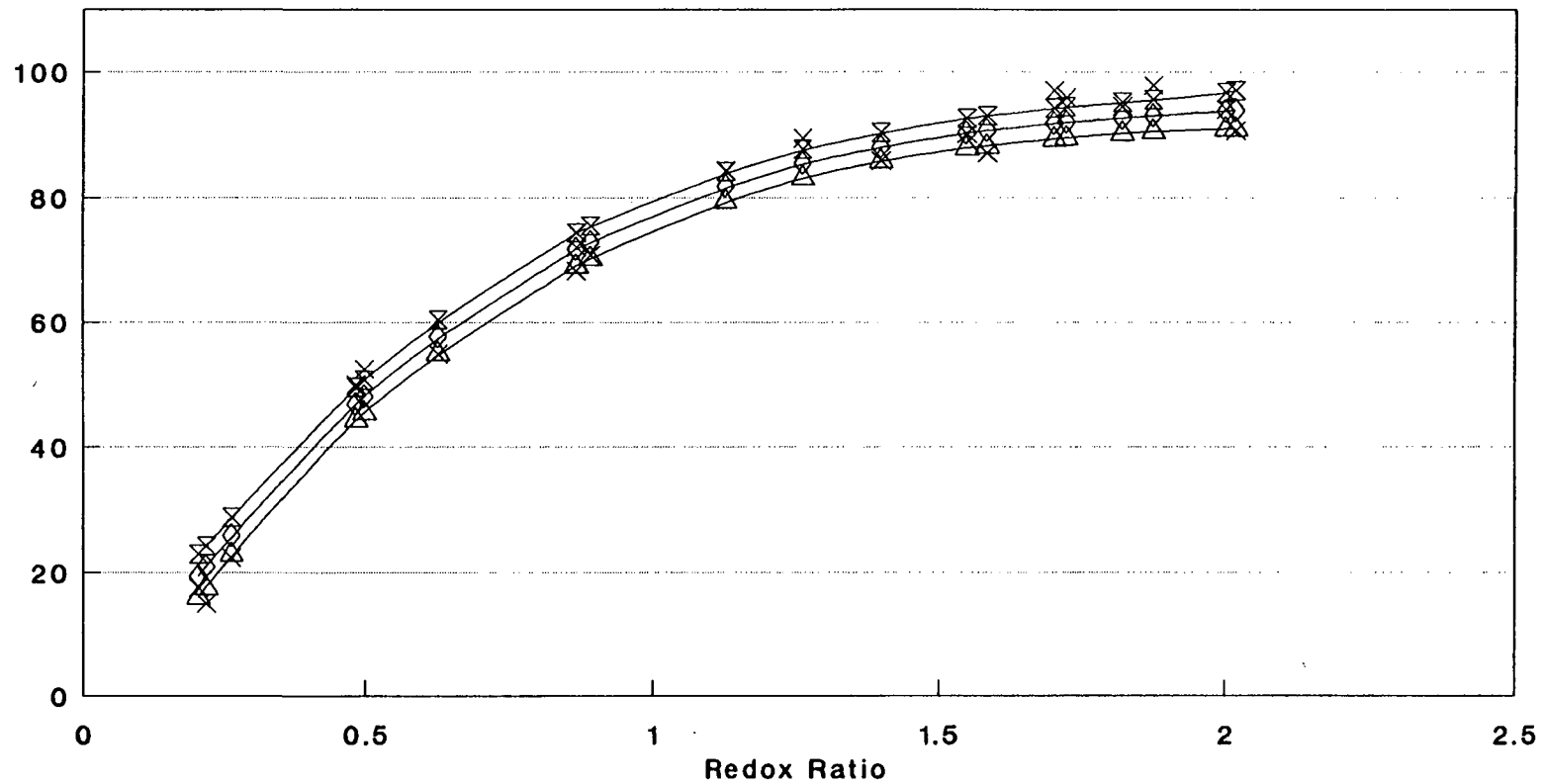


CLEAR FUEL

• Data Points    + Best Fit Line    \* Lower 95% C.L.    □ Upper 95% C.L.

Data for Car No.'s 2, 3, 5 → Clear

**Figure 18**  
**Nitrogen Oxide Conversion Eff., Percent**  
**Ford Taurus 3.0 I**

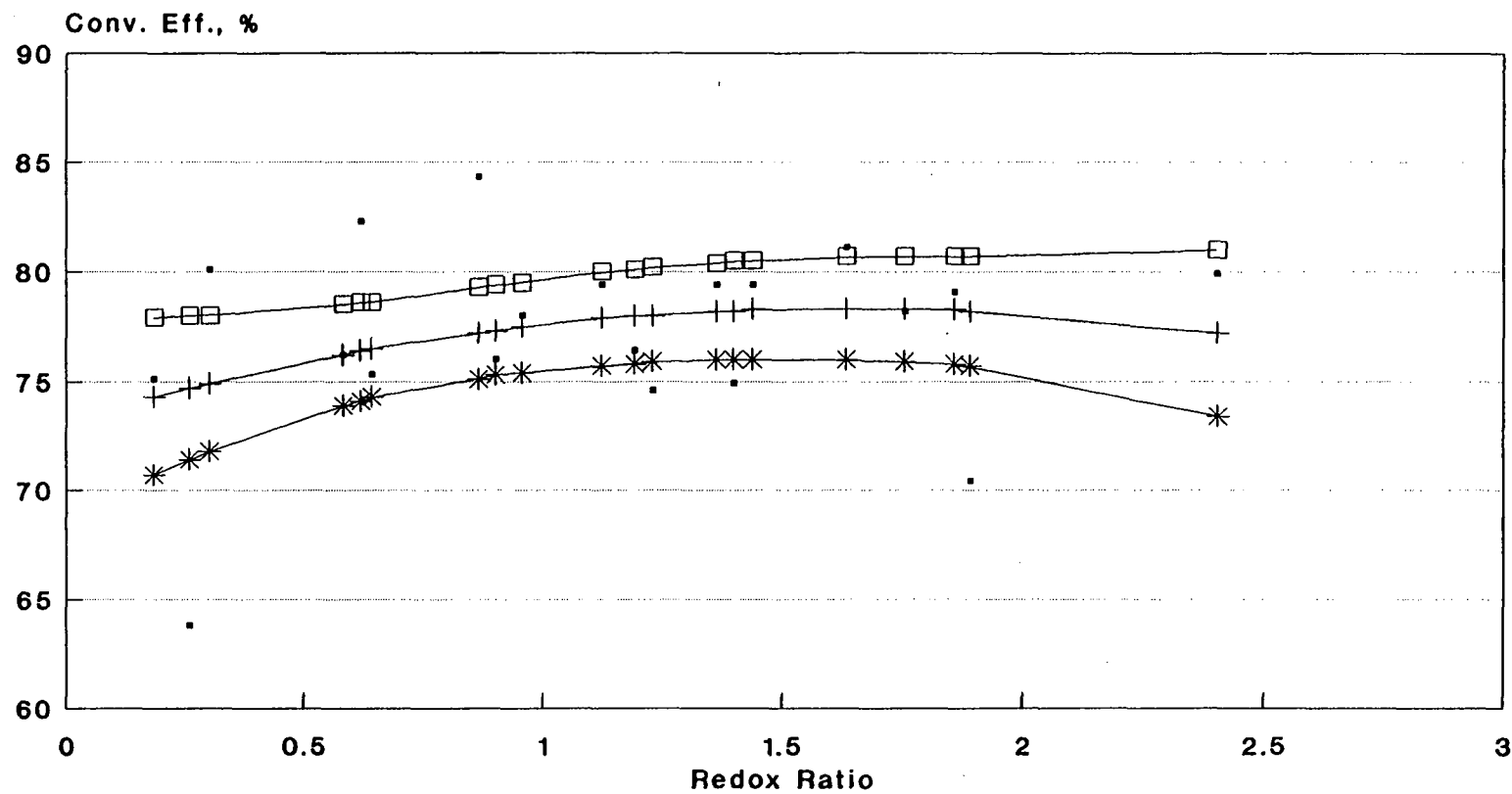


**HiTEC 3000 FUEL**

× Data Points    ◇ Best Fit Line    △ Lower 95% C.L.    ✕ Upper 95% C.L.

Data for Car No.'s 1, 4, 6 → HiTEC 3000

Figure 19  
Hydrocarbon Conversion Eff., Percent  
Ford Escort 1.9 l



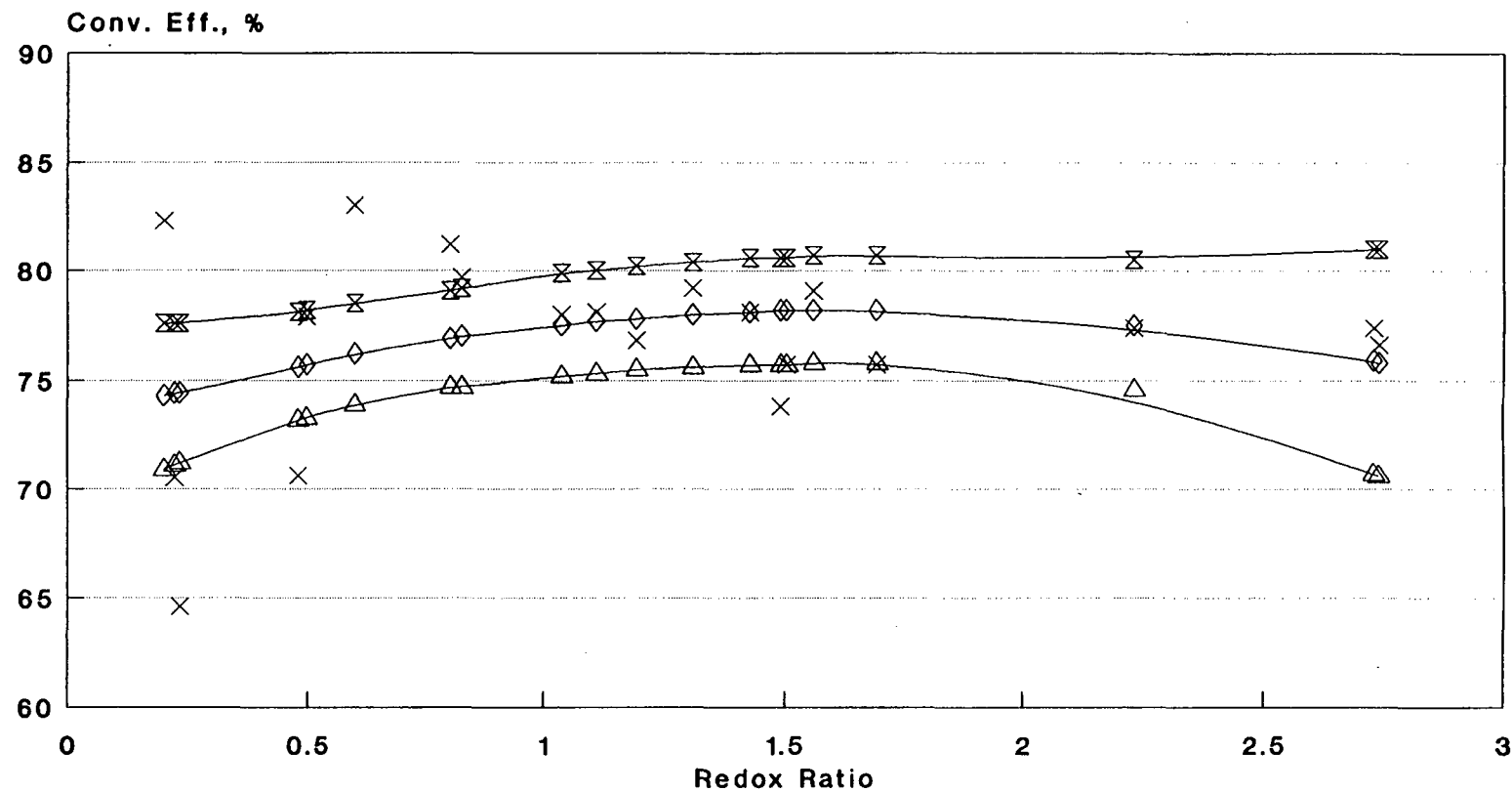
CLEAR FUEL

• Data Points    + Best Fit Line    \* Lower 95% C.L.    □ Upper 95% C.L.

Data for Car No.'s 2, 3, 4 → Clear



Figure 20  
Hydrocarbon Conversion Eff., Percent  
Ford Escort 1.9 l

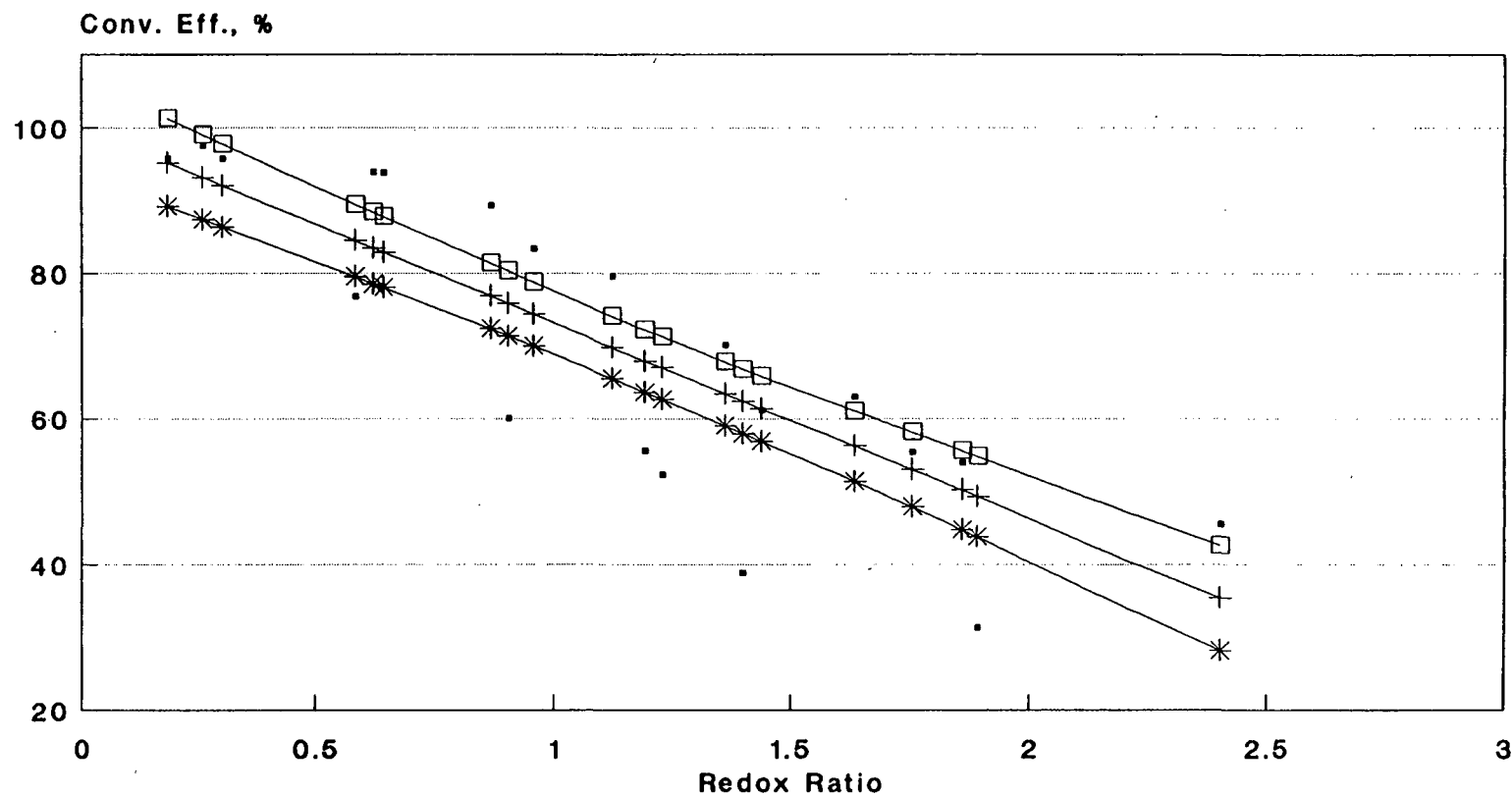


HiTEC 3000 FUEL

× Data Points    ◇ Best Fit Line    △ Lower 95% C.L.    ⊠ Upper 95% C.L.

Data for Car No.'s 1, 5, 6 → HiTEC 3000

Figure 21  
Carbon Monoxide Conversion Eff., Percent  
Ford Escort 1.9 l

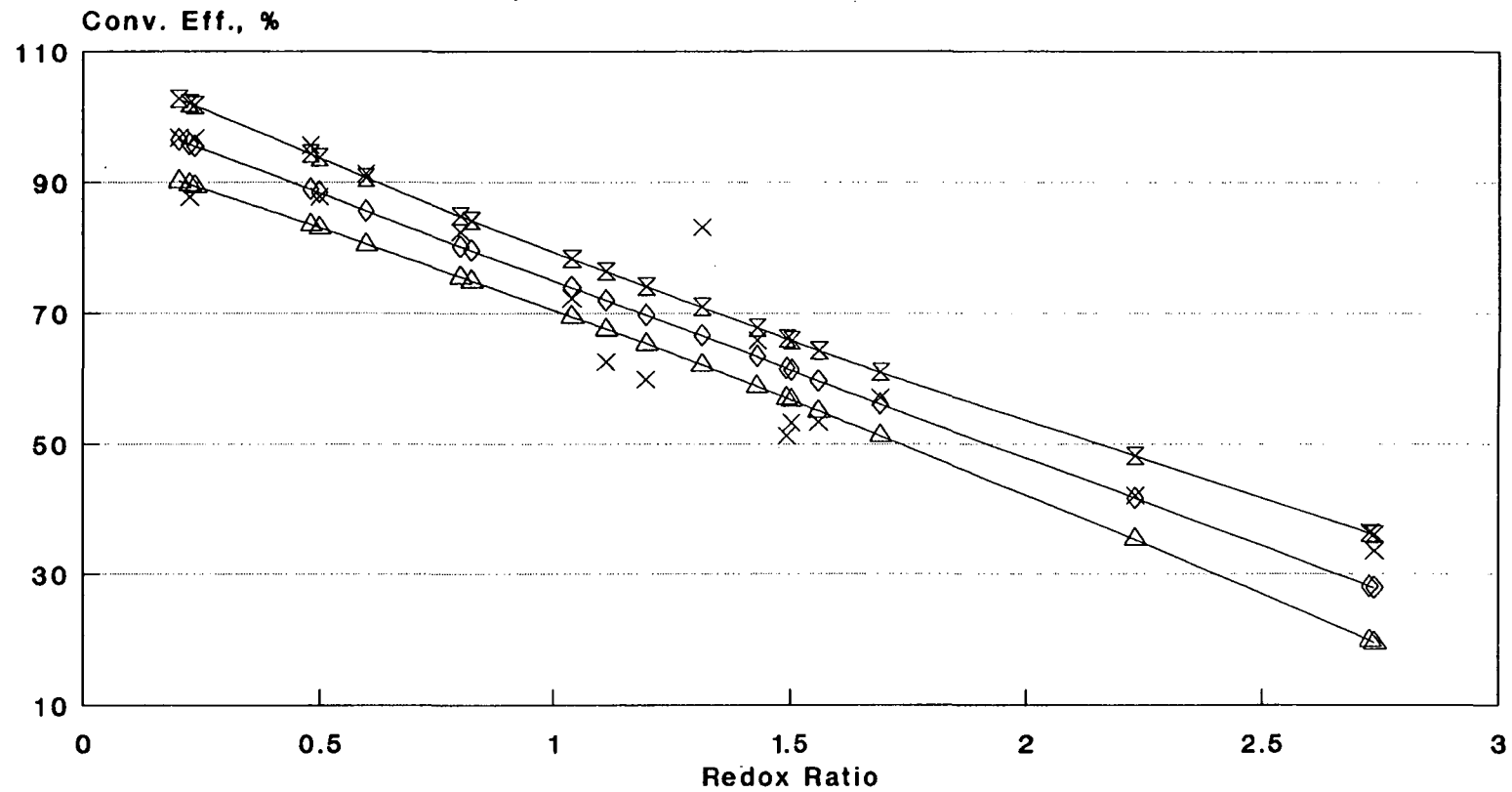


CLEAR FUEL

• Data Points    + Best Fit Line    \* Lower 95% C.L.    □ Upper 95% C.L.

Data for Car No.'s 2, 3, 4 → Clear

**Figure 22**  
Carbon Monoxide Conversion Eff., Percent  
Ford Escort 1.9 l

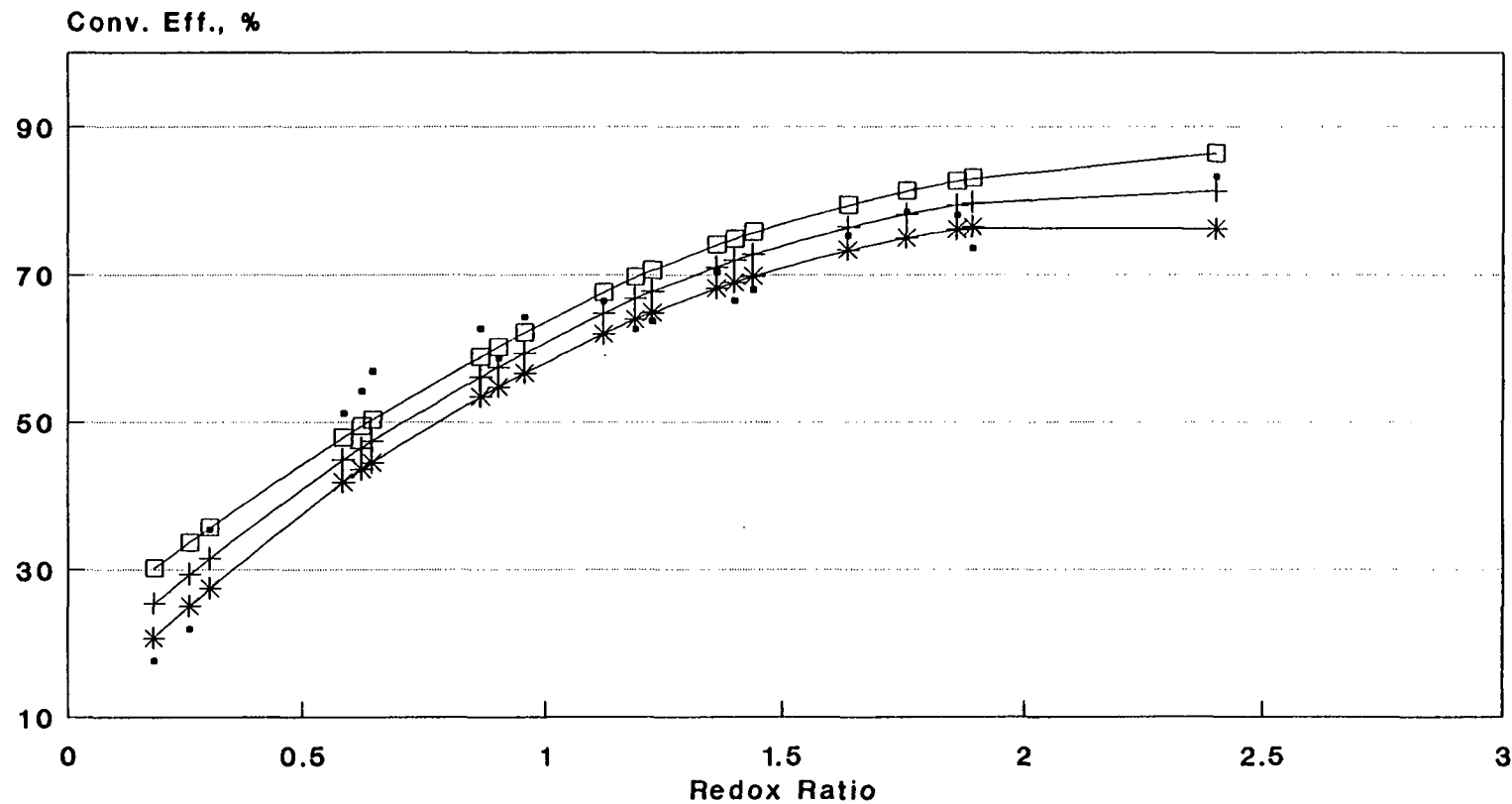


**HiTEC 3000 FUEL**

× Data Points    ◇ Best Fit Line    △ Lower 95% C.L.    ✕ Upper 95% C.L.

Data for Car No.'s 1, 5, 6 → HiTEC 3000

**Figure 23**  
**Nitrogen Oxide Conversion Eff., Percent**  
**Ford Escort 1.9 l**

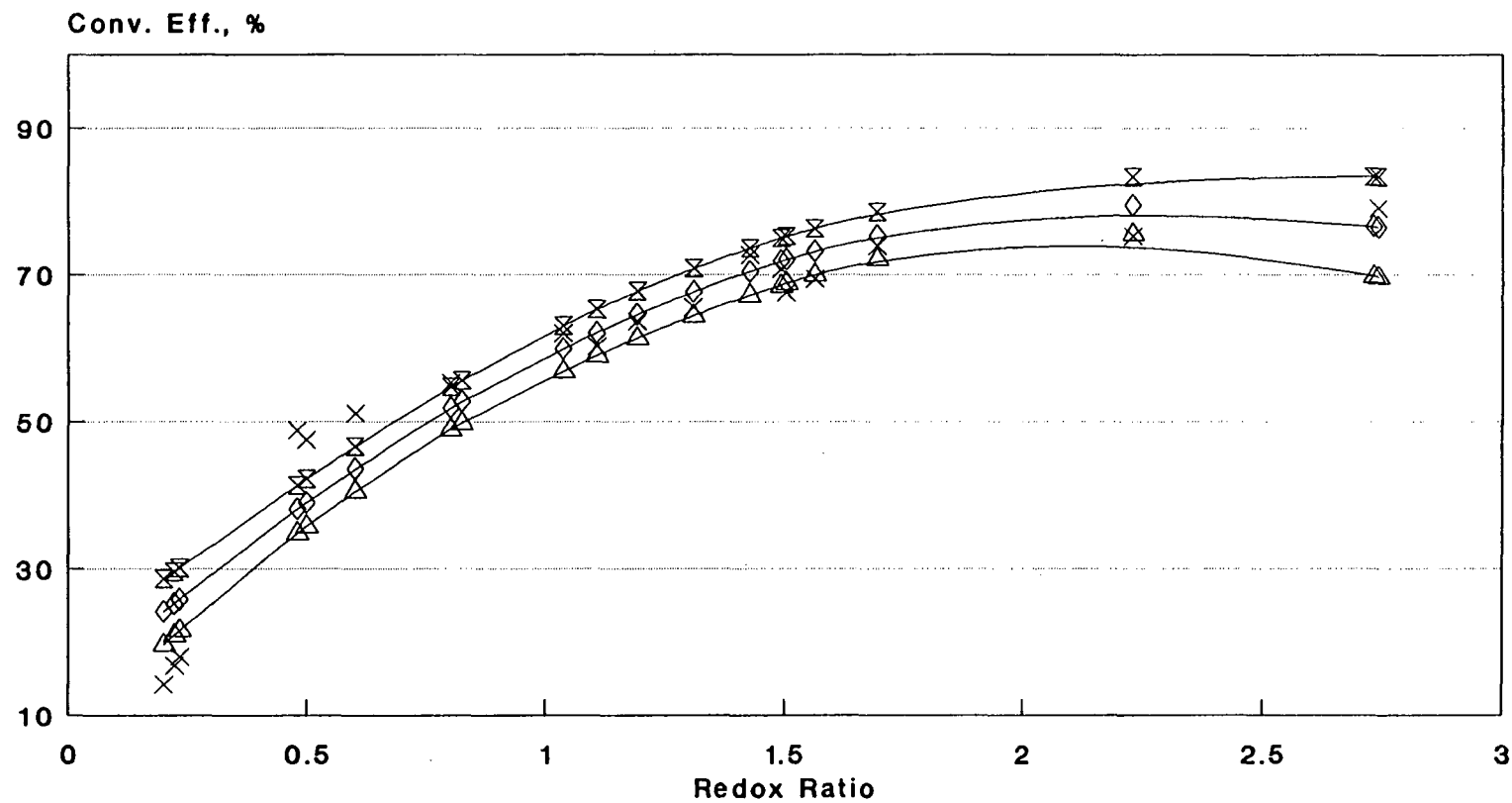


**CLEAR FUEL**

• Data Points    + Best Fit Line    \* Lower 95% C.L.    □ Upper 95% C.L.

Data for Car No.'s 2, 3, 4 → Clear

Figure 24  
Nitrogen Oxide Conversion Eff., Percent  
Ford Escort 1.9 l

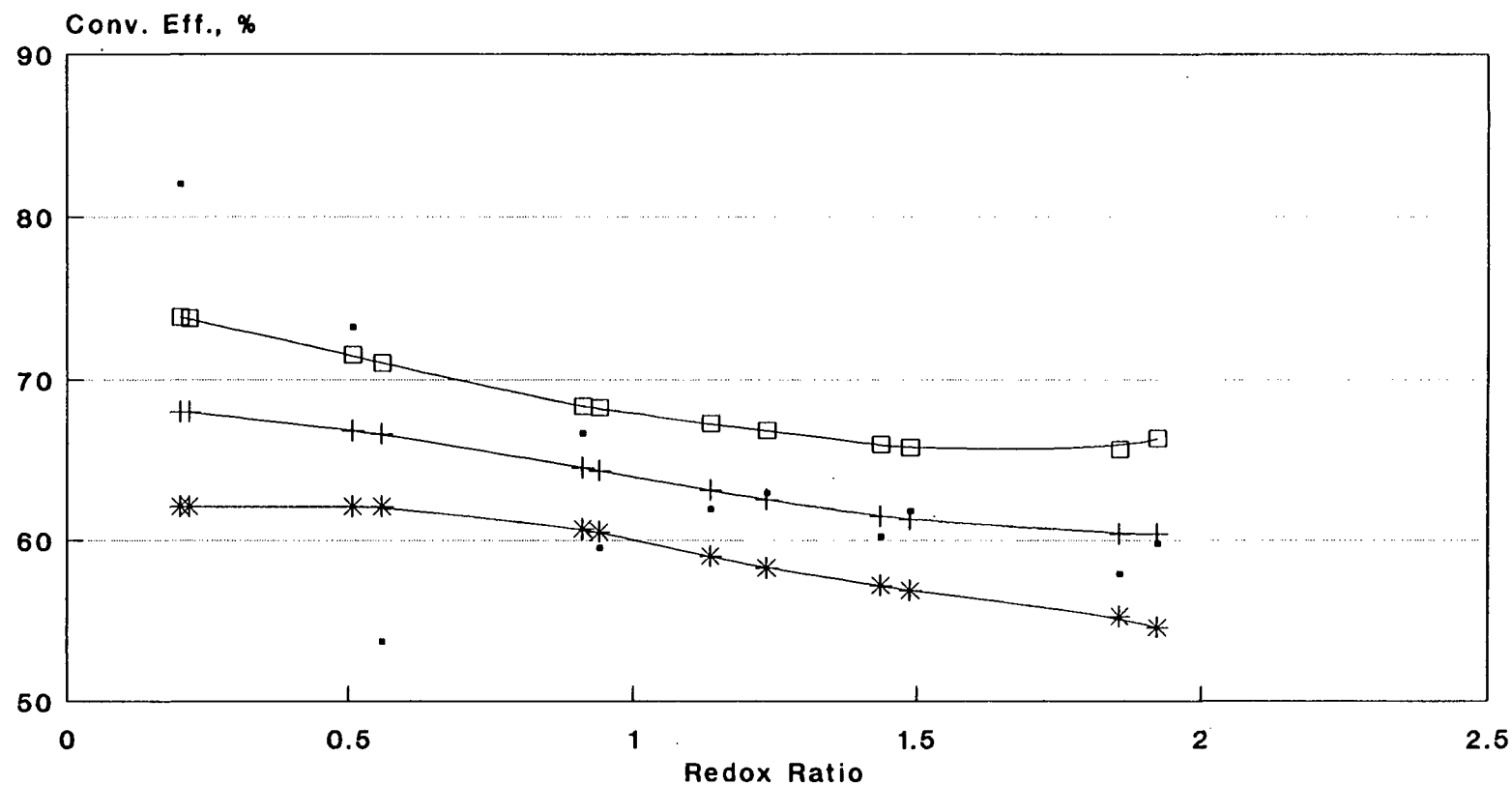


**HITEC 3000 FUEL**

× Data Points    ◇ Best Fuel Line    △ Lower 95% C.L.    ⊗ Upper 95% C.L.

Data for Car No.'s 1, 5, 6 → HITEC 3000

Figure 25  
Hydrocarbon Conversion Eff., Percent  
Ford Crown Victoria 5.0 I

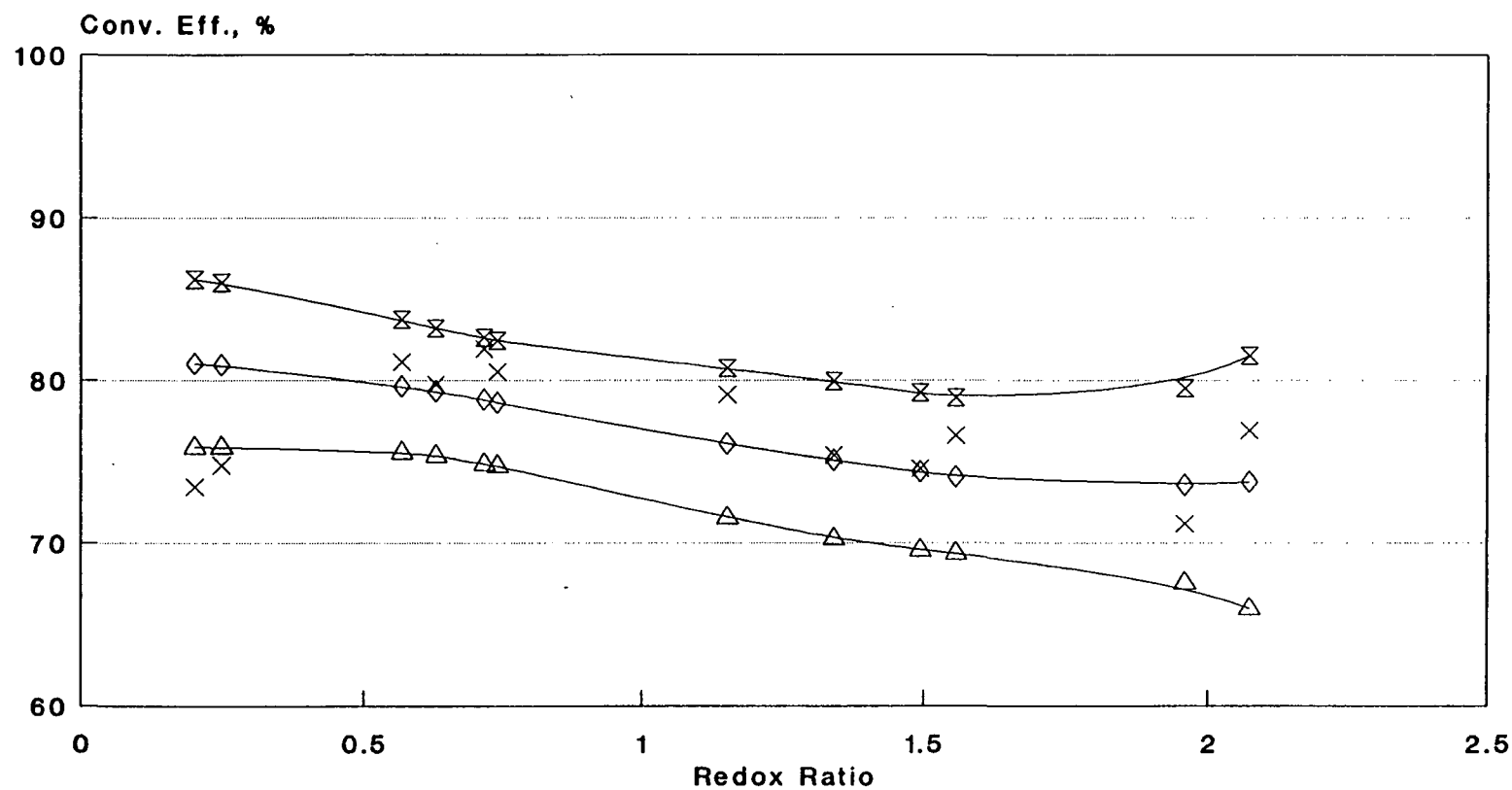


CLEAR FUEL

• Data Points    + Best Fit Line    \* Lower 95% C.L.    □ Upper 95% C.L.

Data for Car No. 6 → Clear

Figure 26  
Hydrocarbon Conversion Eff., Percent  
Ford Crown Victoria 5.0 I

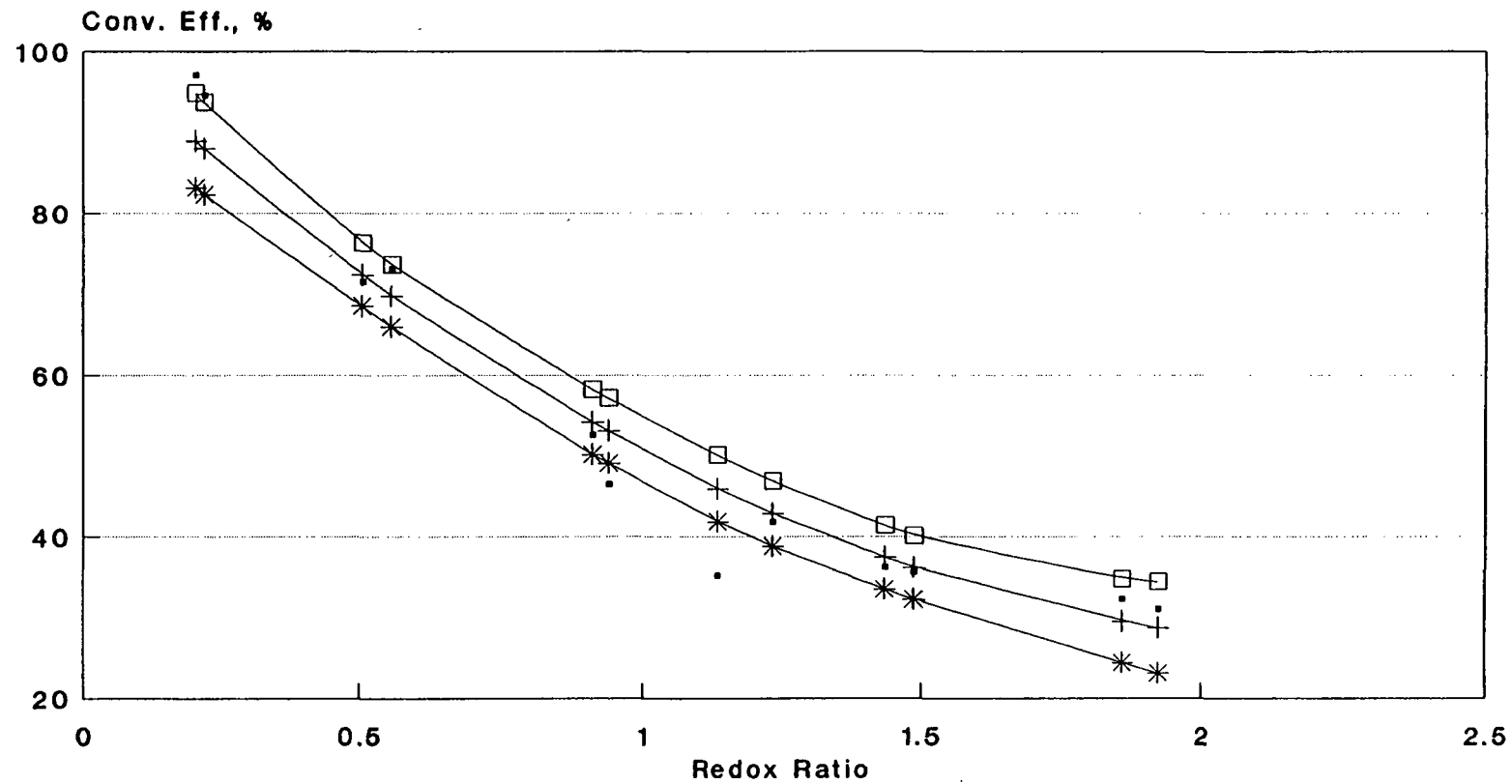


HiTEC 3000 FUEL

× Data Points    ◇ Best Fit Line    △ Lower 95% C.L.    ✕ Upper 95% C.L.

Data for Car No. 2 → HiTEC 3000

**Figure 27**  
**Carbon Monoxide Conversion Eff., Percent**  
**Ford Crown Victoria 5.0 l**



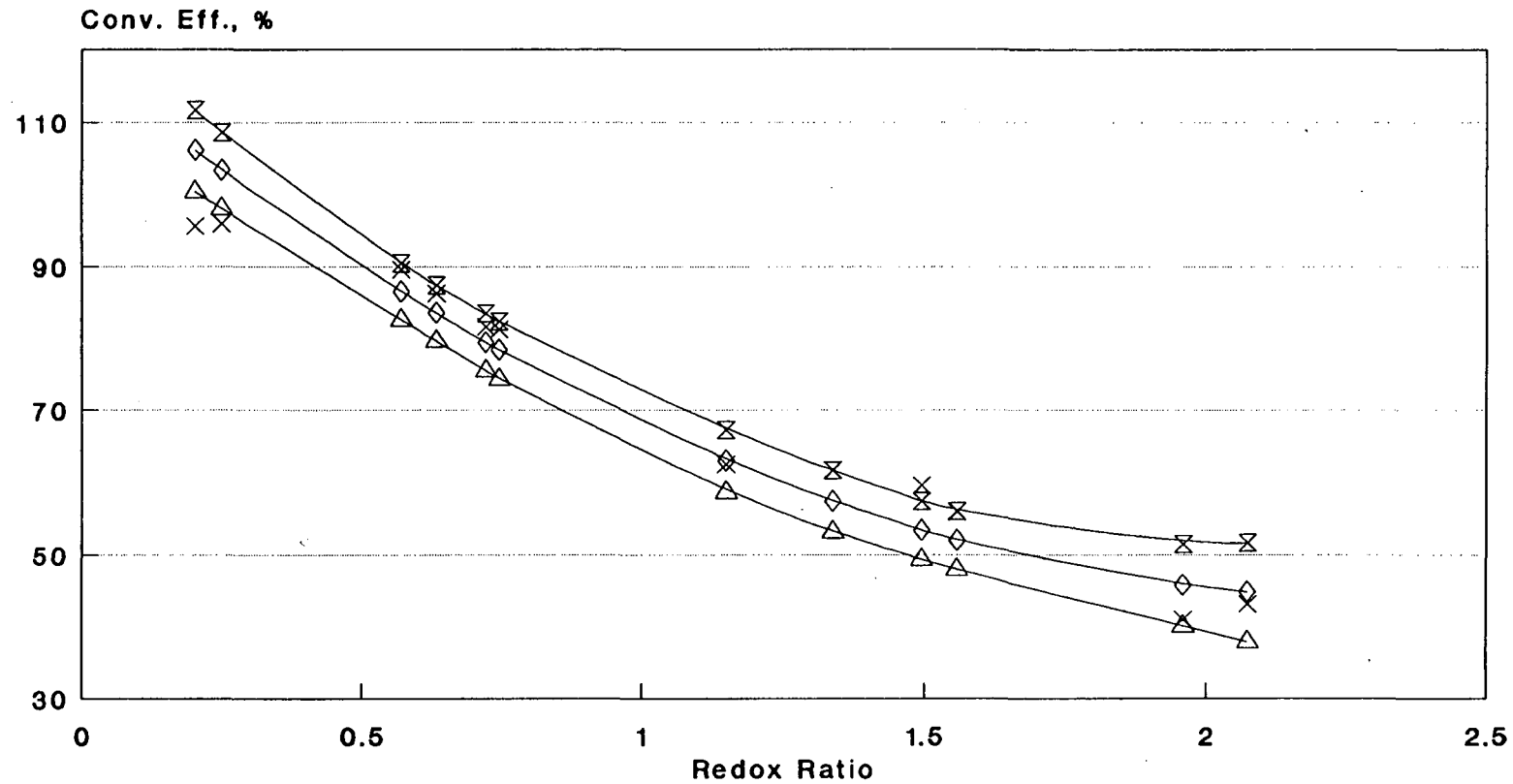
**CLEAR FUEL**

• Data Points    + Best Fit Line    \* Lower 95% C.L.    □ Upper 95% C.L.

Data for Car No. 6 → Clear



**Figure 28**  
Carbon Monoxide Conversion Eff., Percent  
Ford Crown Victoria 5.0 l

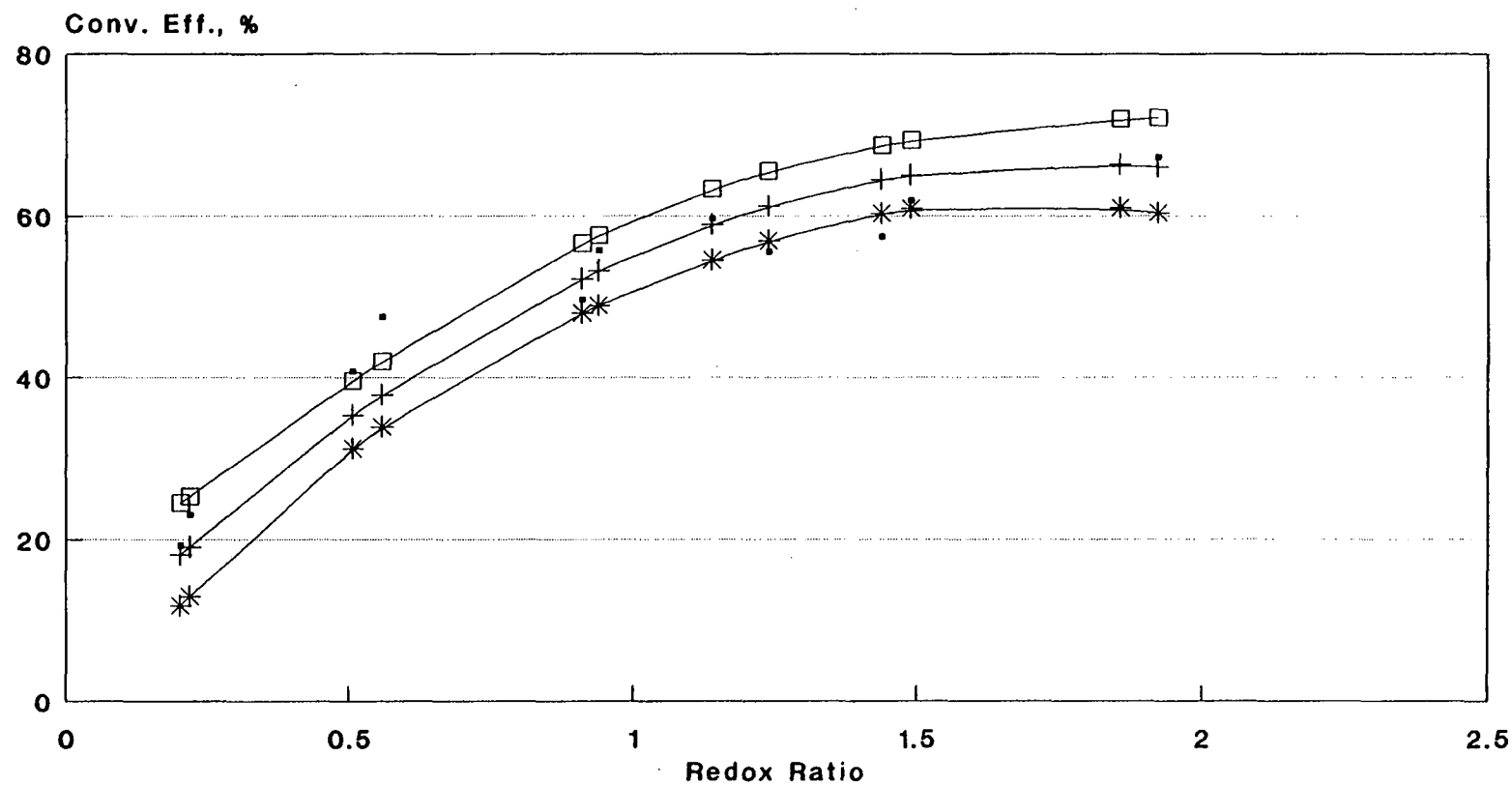


**HiTEC 3000 FUEL**

× Data Points    ◇ Best Fit Line    △ Lower 95% C.L.    ✕ Upper 95% C.L.

Data for Car No. 2 → HiTEC 3000

Figure 29  
Nitrogen Oxide Conversion Eff., Percent  
Ford Crown Victoria 5.0 l

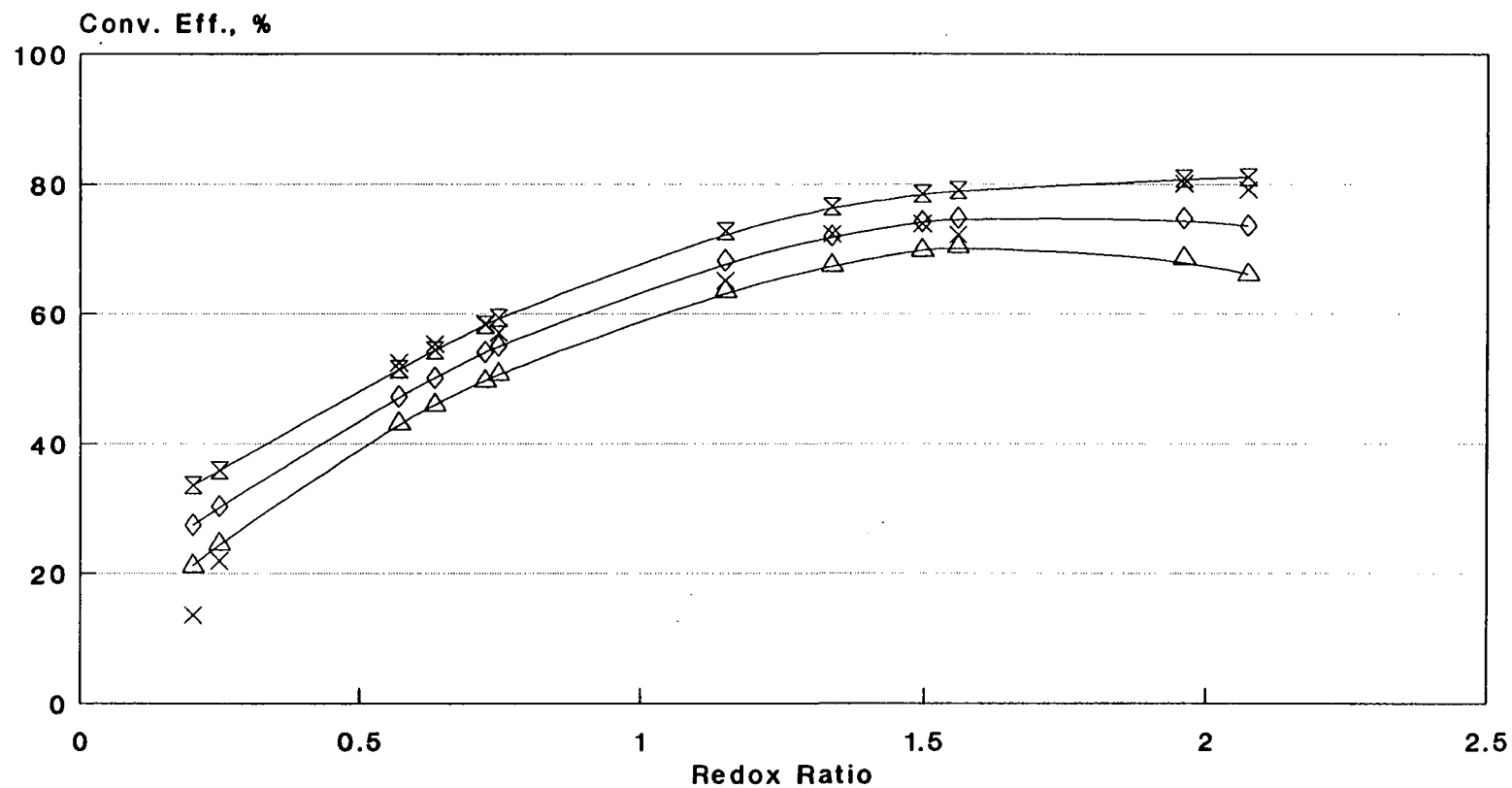


CLEAR FUEL

• Data Points    + Best Fit Line    \* Lower 95% C.L.    □ Upper 95% C.L.

Data for Car No. 6 => Clear

**Figure 30**  
**Nitrogen Oxide Conversion Eff., Percent**  
**Ford Crown Victoria 5.0 l**



**HITEC 3000 FUEL**

× Data Points    ◇ Best Fit Line    △ Lower 95% C.L.    ⊠ Upper 95% C.L.

Data for Car No. 2 → HITEC 3000

## HIGH SPEED CORVETTE CATALYST DURABILITY TEST

Ethyl Corporation ("Ethyl") had previously tested two 1989 Ford 5.0 liter Crown Victorias in an 80 mph "catalyst durability test" using fuel with and without 0.03125 grams per gallon of manganese as the HiTEC 3000 Performance Additive ("HiTEC 3000"). The results showed no indication of plugging of the warm-up catalysts which are closely coupled to the car exhaust manifolds.<sup>(1)</sup>

In order to confirm these results with a high performance GM car, Ethyl operated two 1990 5.7 liter V8 Corvettes on the TRC (Transportation Research Center) test track at 100 mph, again using fuel with and without HiTEC 3000. The tests lasted 25,000 miles and again showed no indication of plugging. It is reasonable to assume that a car could not be operated in normal service in such a manner, so this should be considered a very severe heavy-duty test.

### Summary

The results of this test showed no detrimental effect of 0.03125 g Mn/gal on catalyst performance in a 25,000-mile test of close-coupled monoliths operated continuously at 100 mph.

### Discussion

Ethyl purchased two 1990 new Chevrolet Corvette cars for a high speed catalyst durability test. Emissions of the cars were determined at the ECS Laboratories in Livonia, Michigan, both prior to high speed testing at TRC in Ohio. One car was operated on TRC's clear base fuel (Super Citron), while the other car used this base fuel + HiTEC 3000 blended to 0.03 g Mn/gal. Fuel inspections for these fuels are shown in Attachment 1.

Exhaust backpressure was measured on the two cars at 4500 rpm and wide open throttle before and after mileage accumulation. A summary of these tests is shown in Table 1.

TABLE 1

High-Speed Car Test  
1990 Corvettes 5.7L V8  
100 mph Driving Schedule

	<u>Miles</u>	<u>Exhaust Backpressure</u> <u>"Hg at 4500 rpm - WOT</u>	
		<u>Run 1</u>	<u>Run 2</u>
Clear Car	0	16.4	16.8
	25000	16.2	16.8
HiTEC 3000 Car	0	16.8	17.0
	25000	17.5	17.7

<sup>(1)</sup> In application for fuel additive waiver filed by Ethyl Corporation under Sec. 211 (f) (4) of the Clean Air Act. May, 1990.

-2-

Both cars are in the same range of backpressure and indicate that no plugging had occurred during this test. Catalyst inlet gas temperature at 100 mph measured at start of test was in the 800-850°C range. This temperature would be much greater than found in normal owner use and may be higher than that found in H.D. truck service where catalysts are used. This inspection was done after the 25,000 mile emission check at the ECS Laboratories. The catalysts were inspected at end of test by use of a Boroscope inserted in the backpressure tap. There was no indication of plugging using this visual inspection technique.

Although emission data are difficult to access on a one car to one car basis, the data indicates that both cars maintained the standards for the 25,000 miles.

Emission data is summarized in Table 2. The test driving report by TRC is shown in Attachment 2.

TABLE 2  
EMISSION CHECKS

1990 Corvettes 5.0L V8  
100 mph Driving Schedule

<u>Car Vin No.</u>	<u>Date</u>	<u>Odom</u>	<u>FTP Emissions, g/mi</u>			<u>MPG</u>
			<u>HC</u>	<u>CO</u>	<u>NOx</u>	
118763	9-19-90	67	0.145	0.191	0.563	15.41
118763	9-10-90	86	0.138	0.198	0.522	16.28
119681	9-19-90	65	0.125	0.626	0.535	16.14
119681	9-10-90	84	0.116	0.325	0.620	16.20
118763	11-5-90	25032	0.187	1.162	0.516	17.83
118763	11-6-90	25050	0.208	1.487	0.625	17.73
119681	11-5-90	25032	0.204	1.040	0.844	17.79
119681	11-6-90	25051	0.209	0.837	0.926	17.78

ATTACHMENT 1

## ANALYTICAL REPORT

901272

FOR

ECS

Denis Lenane  
12257 Market Street  
Livonia, MI 48150

11/28/90



## CORE LABORATORIES

LABORATORY TESTS RESULTS  
11/20/90

UNION: 901272

CUSTOMER: EGB

ATTN: Danilo Lenard

T.D.: Sample ID: Supor Cotron

SAMPLED: 10/29/90

SAMPLED: 00:00

DESCRIPTION: Sample ID: Supor Cotron Tank No. 20

LABORATORY I.D.: 901272-0001

DATE RECEIVED: 11/16/90

TIME RECEIVED: 16:00

REMARKS: 1st gal con

DESCRIPTION	FINAL RESULT	LIMITS/DILUTION	UNITS OF MEASURE	TEST METHOD	DATE	TECHN
Viscosity - Gasoline		0.1		ASTM D86	11/20/90	JHE
Initial Boiling Point	78	1	000. F	ASTM D86		
5% Evaporated Temperature	93	1	000. F	ASTM D86		
10% Evaporated Temperature	107	1	000. F	ASTM D86		
15% Evaporated Temperature	123	1	000. F	ASTM D86		
20% Evaporated Temperature	140	1	000. F	ASTM D86		
25% Evaporated Temperature	163	1	000. F	ASTM D86		
30% Evaporated Temperature	199	1	000. F	ASTM D86		
35% Evaporated Temperature	258	1	000. F	ASTM D86		
40% Evaporated Temperature	291	1	000. F	ASTM D86		
45% Evaporated Temperature	304	1	000. F	ASTM D86		
50% Evaporated Temperature	327	1	000. F	ASTM D86		
55% Evaporated Temperature	360	1	000. F	ASTM D86		
End Point	402	1	000. F	ASTM D86		
8 Overhead Recovery	96.6	0.001	%	ASTM D86		
8 Residue	1.1	0.1	%	ASTM D86		
8 Loss	2.3	0.01	%	ASTM D86		
Refractive Index Anisotropy		0.1		ASTM D1319	11/20/90	ELH
Saturated	37.6	0.1	L.V.X	ASTM D1319		
Unsaturated	0.3	0.1	L.V.X	ASTM D1319		
Aromatic	42.1	0.1	L.V.X	ASTM D1319		
NO Number		0.1		ASTM D2699, 2700	11/21/90	OLP
Research Octane Number (Gasoline)	95.8	0.1	0.1 Octane No.	ASTM D2699		
Motor Octane Number (Gasoline)	86.6	0.1	0.1 Octane No.	ASTM D2700		
(Research + Motor)/2	91.1	0.1	0.1 Octane No.	ASTM D2699, D2700		
1 Sulfur by Microcoulometry	29	1	ppm wt.	ASTM D3120	11/20/90	LAB
1 Producers, Reid	10.8	0.1	psi	ASTM D323	11/20/90	PEL
Consent, Hooked	1.6	0.1	mg/100ml	ASTM D321	11/20/90	ELH
Consent, Unhooked	88.6	0.1	mg/100ml	ASTM D321	11/20/90	ELH
1 in Gasoline by AA	<0.001	0.001	g/gal	ASTM D-3237	11/20/90	KRK
1000 in Gasoline by AA	0.002	0.001	g/gal	ASTM D3831	11/20/90	KRK

APPROVED BY:

 12649 Richfield Court  
 Livonia, MI 48150  
 (313) 662-3900





## CORE LABORATORIES

LABORATORY TEST RESULTS  
11/28/90

NUMBER: 901272 CUSTOMER: ECS

ATTN: Denis Lenane

MT I.D.: Sample ID: Super Cetron W/Add  
 SAMPLED: 10/25/90  
 SAMPLED: 00:00  
 DESCRIPTION: Sample ID: Super Cetron Tank No. 15

LABORATORY I.D.: 901272-0002  
 DATE RECEIVED: 11/16/90  
 TIME RECEIVED: 16:00  
 REMARKS: 1st gal can

DESCRIPTION	FINAL RESULT	LIMITS/DILUTION	UNITS OF MEASURE	TEST METHOD	DATE	TECHN
Distillation - Gasoline		%		ASTM D86	11/20/90	JME
Initial Boiling Point	76	1	Deg. F	ASTM D86		
0% Evaporated Temperature	94	1	Deg. F	ASTM D86		
10% Evaporated Temperature	105	1	Deg. F	ASTM D86		
20% Evaporated Temperature	121	1	Deg. F	ASTM D86		
30% Evaporated Temperature	137	1	Deg. F	ASTM D86		
40% Evaporated Temperature	161	1	Deg. F	ASTM D86		
50% Evaporated Temperature	196	1	Deg. F	ASTM D86		
60% Evaporated Temperature	252	1	Deg. F	ASTM D86		
70% Evaporated Temperature	287	1	Deg. F	ASTM D86		
80% Evaporated Temperature	303	1	Deg. F	ASTM D86		
90% Evaporated Temperature	322	1	Deg. F	ASTM D86		
95% Evaporated Temperature	342	1	Deg. F	ASTM D86		
End Point	399	1	Deg. F	ASTM D86		
% Overhead Recovery	97.6	0.001	%	ASTM D86		
% Residue	1.4	0.1	%	ASTM D86		
% Loss	1.0	0.01	%	ASTM D86		
Fluorescent Indicator Adsorption		%		ASTM D1319	11/20/90	ELM
Saturates	56.3	0.1	L.V.X	ASTM D1319		
Olefins	0.9	0.1	L.V.X	ASTM D1319		
Aromatics	43.2	0.1	L.V.X	ASTM D1319		
Octane Numbers		%		ASTM D2699, 2700	11/21/90	DLP
Research Octane Method(Gasoline)	96.4	0.1	0.1 Octane No.	ASTM D2699		
Motor Octane Method(Gasoline)	87.0	0.1	0.1 Octane No.	ASTM D2700		
(Research + Motor)/2	91.7	0.1	0.1 Octane No.	ASTM D2699, D2700		
Total Sulfur by Microcoulometry	17	1	ppm wt.	ASTM D3120	11/20/90	LAB
Vapor Pressure, Reid	10.85	0.1	PSI	ASTM D323	11/20/90	PEL
Water Content, Washed	1.0	0.1	mg/100ml	ASTM D-381	11/20/90	ELM
Water Content, Unwashed	105.8	0.1	mg/100ml	ASTM D381	11/20/90	ELM
Asphaltenes in Gasoline by AA	0.001	0.001	g/gal	ASTM D-3237	11/20/90	KRK
Inorganics in Gasoline by AA	0.027	0.001	g/gal	ASTM D3831	11/20/90	KRK

APPROVED BY:

12649 Richfield Court  
 Livonia, MI 48150  
 (313) 462-3900

## ATTACHMENT 2

ECS

Corvette High Speed Tests  
(For Fuel Additive Comparison)

Conducted By:

THE TRANSPORTATION RESEARCH CENTER OF OHIO  
East Liberty, Ohio 43319

Date: November, 1990  
Project #: 090435/1000  
Type of Report: Final  
Prepared For: Mr. Doug Smith  
Engine & Control Systems, Inc.  
12011 Market Street  
Livonia, MI 48150

ECS.FR/FPPFINALS/nmw

## NOTICE

The Transportation Research Center of Ohio does not endorse or certify products of manufacturers. The manufacturer's name appears solely to identify the test article. The Transportation Research Center assumes no liability for the report or use thereof. It is responsible for the facts and the accuracy of the data presented herein. This report does not constitute a standard, specification, or regulation.

Report Prepared By:

Randall A. Sanders  
Project Engineer

Date 11-30-90

Report Approved By:

Kay Latimer  
Project Manager

Date 11-29-90

## TABLE OF CONTENTS

<u>Section</u>	<u>Title</u>	<u>Page</u>
	Notice	1
	Table of Contents	ii
1.0	Objective	1
2.0	Approach	1
3.0	Vehicle Documentation	1
4.0	Results Summary	2
5.0	Procedure and Results Detail	2

### 1.0 OBJECTIVE

The purpose of this test was to observe the effects of a fuel additive on exhaust system back pressure and emissions output. These effects were also compared with a non-additive fuel.

### 2.0 APPROACH

ECS requested that 25,000 miles be accumulated as quickly as possible on two new ECS provided Corvettes. Accordingly, the two Corvettes were driven continuously at 100 mph on TRC's high speed test track.

### 3.0 VEHICLE DOCUMENTATION

TRC Vehicle #716

1990 Chevrolet Corvette (Red)

5.7L. Fuel Injection V-8 Piston

(2 Valve)

4 Speed Automatic Transmission

VIN. 1G1YY2383L5118763

Control Fuel

TRC Vehicle # 717

1990 Chevrolet Corvette (white)

5.7 Fuel injection V-8 Piston

(2 Valve)

4 Speed Automatic Transmission

VIN. 1G1YY2386L5119681

Test Fuel

ENGINE & CONTROL SYSTEMS, INC.  
NOVEMBER, 1990  
PROJ. NO. 90435

1 Corvette High Speed Tests  
(For Fuel Additive Comparison)

#### 4.0 RESULTS SUMMARY

The average total mileage accumulation (for both vehicles).

= 24,747 miles

% @ 100 mph	-	88.9
% @ 70 mph	-	1.2
% @ 80 mph	-	3.1
% during construction	-	<u>6.8</u>
		100.0

Vehicle #716 accumulated 24,597 miles and used 1,427.0 gallons of fuel.

Fuel = 17.24 mi/gal

Vehicle #717 accumulated 24,897 miles and used 1,467.6 gallons of fuel.

Fuel = 16.96 mi/gal

#### 5.0 PROCEDURE AND RESULTS DETAIL

##### 5.1 Pre-Test

On November 10, 1990, TRC received two 1990 Chevrolet Corvettes from ECS. These vehicles were used for a fuel additive test for Ethyl Corporation.

Both vehicles were subjected to TRC's standard incoming safety inspection with the addition of white strobe lamps placed in the front license plate fascia. The strobe lamps were used to alert other traffic of the high speed test vehicles.

ENGINE & CONTROL SYSTEMS, INC.  
NOVEMBER, 1990  
PROJ. NO. 90435

2 Corvette High Speed Tests  
(For Fuel Additive Comparison)

A TRC driver plus an Ethyl Corporation representative performed several steady state and wide open throttle acceleration instrumented test runs to measure exhaust back pressure and catalytic converter temperature. The results were obtained and retained by Ethyl personnel.

#### 5.2 Test

Both vehicles were to be driven at a constant 100 mph until each vehicle's odometer indicated 25,000 miles. The vehicles stopped for driver safety breaks, fuel additions, service stops, or until weather/track conditions necessitated going below 70 mph. All accelerations were moderate.

#### 5.3 Post-Test

After each vehicle exceeded 25,000 odometer indicated miles, Ethyl personnel plus a TRC driver repeated instrumented testing from the pre-test segment to observe any change from mileage accumulation. These results were obtained and retained by Ethyl personnel.

#### 5.4 Fuel Handling and Storage

The test was run using Sohio (BP) Super Cetron (92 R+M/2 Oct.) as the control fuel and Super Cetron plus the Ethyl Corporation supplied additive as the test fuel. The test fuel was blended at a ratio of 500 gallons Super Cetron to one pint of additive. The test fuel was blended by placing the additive into an empty or near empty storage tank and adding 500 gallons of Super Cetron on top of the additive.

Then, 30 gallons of the blended test fuel were pumped back into itself. Finally, a four tenths of a gallon sample was pumped out, placed in a clean container, and sent to ECS. The control fuel was handled in the same manner minus the inclusion of the additive. A slight deviation to the above procedure was made when TRC made available a 1,050-gallon storage tank as opposed to the original 550-gallon tank. In this case two pints of additive were placed into the tank and 1,000 gallons of fuel were added. The 1,050-gallon tank made blending fuel less frequent. Additionally, both test fuel tanks were steamed cleaned and new pump filters were added prior to filling.

NOTES: Unit #717 struck a small animal on two separate occasions resulting in a cracked front spoiler. Unit #716 struck a small animal once resulting in a broken front spoiler and deformed power steering cooler, A/C condenser, and radiator. Both units continued testing after a visual safety examination. On 11/2/90 both vehicles were trucked away by ECS personnel. Exit mileage #716 - 25,024 and #717 - 25,021.



BEFORE THE  
UNITED STATES  
ENVIRONMENTAL PROTECTION AGENCY

IN RE APPLICATION FOR A FUEL )  
ADDITIVE WAIVER FILED BY )  
ETHYL CORPORATION UNDER )  
§ 211(f)(4) OF THE CLEAN AIR )  
ACT )

COMMENTS IN SUPPORT OF THE WAIVER APPLICATION  
FOR THE HITEC® 3000 PERFORMANCE ADDITIVE

Submitted by:

ETHYL CORPORATION  
P.O. BOX 2189  
RICHMOND, VA 23217

Of Counsel:

Hunton & Williams  
2000 Pennsylvania Ave., N.W.  
P.O. Box 19230  
Washington, D.C. 20036  
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Ray Wilkins, Jr.  
Senior Vice President  
Ethyl Corporation  
P.O. Box 2189  
Richmond, VA 23217

July 23, 1990

### SUMMARY

On May 9, 1990, Ethyl Corporation ("Ethyl") filed a fuel additive waiver application under § 211(f)(4) of the Clean Air Act ("CAA" or "Act"), for use of the HiTEC® 3000 Performance Additive (the "Additive") at a concentration of 0.03125 grams of manganese per gallon in unleaded gasoline. Since submittal of the waiver application, a limited number of comments have been filed with the Environmental Protection Agency ("EPA" or "Agency") suggesting that use of the Additive could have public health implications. This document and its appendices address the health issue in detail. In particular, they show that use of the Additive would cause significant reductions in emissions of nitrogen oxides (NOx), carbon monoxide (CO), reactive hydrocarbons (HC), formaldehyde and aromatics, such as benzene, while causing no discernable change in environmental loadings of manganese.

These comments also supplement the material presented in Ethyl's waiver application showing that the Additive (1) would reduce NOx and CO emissions, while having no practical effect on HC emissions; (2) would not cause catalyst plugging; (3) would be fully compatible with reformulated fuels; (4) would complement the use of oxygenates; and (5) would not adversely affect compliance with more stringent mobile source standards.

-2-

I. USE OF THE ADDITIVE WILL PROMOTE THE PUBLIC HEALTH AND WELFARE, AND THE PRODUCTIVE CAPACITY OF THE NATION.

The principal showing required of a waiver applicant under § 211(f)(4) of the Act is that an additive "not cause or contribute to a failure of any emission control device or system . . . to achieve compliance . . . with the emission standards" for which automobiles are certified. As described in its waiver application, Ethyl has met this requirement by conducting the most comprehensive fuel additive test program ever undertaken by a waiver applicant. To date, no commentator has submitted any analyses or new data refuting this conclusion.

In contrast to the "cause or contribute" standard, neither § 211(f)(4) of the Act nor its legislative history mention public health. Indeed, EPA itself has said that while emissions "of unregulated pollutants are of continuing interest to EPA [under other provisions of the Act] due to their potential adverse effect on health . . . [such considerations] have no bearing on . . . [a] waiver decision."<sup>1/</sup>

However, even though public health is not relevant to § 211(f)(4) considerations, Ethyl addressed at length the public health effects of use of the Additive<sup>2/</sup> to establish that approval of its application would promote the overall objectives

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<sup>1/</sup> In Re Application for MTBE, Decision of the Administrator at 4, n.5 (December 26, 1978) (emphasis added).

<sup>2/</sup> See Ethyl Waiver Application at 60-69, and Appendices 7 & 8.

-3-

of the Clean Air Act.<sup>3/</sup> Ethyl showed that widespread use of the Additive would reduce emissions of noxious pollutants by up to 1.7 billion pounds per year, while not materially changing environmental levels of manganese. With respect to manganese specifically, the waiver application showed that the metal is nutritionally essential and has been extensively studied by EPA and other independent scientific bodies, all of which concluded that manganese emissions of orders of magnitude higher than those associated with use of the Additive would not cause adverse public health effects.<sup>4/</sup>

Because Ethyl has presented a sound basis for the Agency to exercise its judgment regarding any public health concerns, the burden is on those who advocate disapproval of the application on health grounds to come forward with evidence addressing the levels of manganese associated with HiTEC 3000 to support their claims. Significantly, no one has disputed that public health benefits would flow from the reductions in NOx, CO, reactive HC, benzene, and formaldehyde emissions associated with use of the Additive. Rather, those who have commented critically on the public health issue have speculated or presented unsubstantiated allegations that adverse effects would occur at environmental levels of manganese which differ insignificantly from those that occur in the natural environment.

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<sup>3/</sup> The overall purpose of the Clean Air Act is "to promote the public health and welfare and the productive capacity" of the Nation's population. CAA § 101(b)(1).

<sup>4/</sup> See Ethyl Waiver Application at 62-69, and Appendix 8.

-4-

As discussed below, a large body of evidence supports the conclusions of EPA and other independent organizations that low levels of manganese present no public health concern.

A. Emissions and Ambient Concentrations of Manganese

Under Ethyl's waiver application, only one drop of the Additive (0.03125 grams) would be used in a gallon of gasoline. Manganese emissions would be extremely small. Based on data developed using EPA's Federal Test Procedure ("FTP") for particulate matter emissions from light duty diesel vehicles, a typical car would emit no more than 0.5 percent of the manganese contained in the Additive, approximately 0.06 grams of manganese annually. Assuming, as a margin of safety, that 30 percent of the manganese burned in the fuel were emitted (as was the case in Ethyl tests of the Additive in older, non-catalyst vehicles), only 3.6 grams would be emitted annually by a typical car.

Even at an emission rate of 30 percent, manganese emissions associated with widespread use of the Additive would amount to little more than one percent of the manganese emitted annually from natural sources (e.g., windblown dust).

1. Manganese in the air

Given the extremely low manganese emissions associated with use of the Additive, concentrations of airborne manganese would not materially differ from current naturally occurring levels. Consider the following:

- Actual monitored concentrations of manganese in Canada, where the Additive has been used for a decade at twice the amount sought in this application, range up to

-5-

approximately 0.04 ug/m<sup>3</sup> in large urban areas. These concentrations are little or no different from those in the United Kingdom, where the Additive has never been used in gasoline.

- o In the United States, the Additive has been used for over two decades in leaded gasoline. Manganese emissions from such use peaked in the mid-1980s. Actual mid-1980s monitored urban ambient concentrations, however, were only about 0.03-0.05 ug/m<sup>3</sup>, again little different than in a country where the Additive has not been used.<sup>5/</sup>
- o Actual ambient monitoring data in California in the mid-1980s in areas with high concentrations of mobile source traffic showed ambient manganese concentrations of about 0.015-0.03 ug/m<sup>3</sup>. The mobile source contribution to these levels, which was estimated based on use of the Additive at levels much higher than proposed in this application, was only about 0.003-0.013 ug/m<sup>3</sup>.

Thus, actual experience shows that the Additive would not discernibly contribute to airborne levels of manganese. Further confirmation is provided by conservative atmospheric modeling, which indicates maximum increases in urban ambient concentrations with use of the Additive in all new cars would be at most approximately 0.017 ug/m<sup>3</sup>, even if one assumes that at least 30 percent of the Additive is emitted to the air.

## 2. Manganese in the soil

Manganese is the twelfth most abundant element in nature. The concentration of manganese in soil ranges up to 7,000 ppm, with an average of about 1,000 ppm. One cubic meter of soil contains on average approximately one kilogram of manganese. If

---

<sup>5/</sup> By comparison, total manganese emissions in 1999 resulting from the Additive's use would range down to 20 times less than the manganese emissions in the mid-1980s, based on Ethyl's particulate matter testing.

-6-

the Additive were used in all unleaded gasoline, the increase in soil concentrations 5 meters from a heavily travelled expressway would be only about 4.6 ppm after 50 years, even if one assumes that 30 percent of the manganese in the Additive is emitted. This is far less than one tenth of one percent of the average concentration of manganese naturally occurring in the soil (about 1,000 ppm).

Viewed another way, a uniform manganese contribution from the Additive of 4.6 ppm to the soil after 50 years would approximately equal the contribution made if one watered his lawn only once a year during this 50 year period (assuming a manganese concentration in water consistent with EPA's standard for drinking water, and a recommended watering rate of one inch). Indeed, the cumulative concentration of manganese in soil at a point five meters from a busy expressway caused by 50 years of use of the Additive would be less than the concentration caused by spilling a cup of tea, one time, at that point (4.6 ppm for soil versus 6.9 ppm for tea). Both comparisons assume that at least 30 percent of the manganese in the Additive is emitted.

Such comparisons (and many more) suggest that natural variation in the manganese content of soil would completely overwhelm any short term or cumulative contribution resulting from use of the Additive.

B. Population exposure to manganese

Health authorities recommend a normal daily intake of manganese of 2,000-5,000 ug, although higher levels are

-7-

recommended for pregnant women, children, and the elderly. On a daily basis, an individual typically takes in 2,000-9,000 ug of manganese through ingestion of food and water, and about 0.8 ug through inhalation. About 120 ug of this typical daily intake is absorbed by the body, given the body's mechanism for regulating manganese uptake.

Exposure to manganese from use of the Additive would not, as a practical matter, change existing exposure levels. For example, assuming a worst-case mobile source contribution to ambient manganese concentrations based on actual monitoring data in California,<sup>6/</sup> SAI, Inc. calculated that the manganese accumulated at the soil's surface for over 70 years as a result of use of the Additive would increase the normal daily intake of manganese by less than one-tenth of one percent. That is, use of the Additive, even after 70 years, would contribute to an increase in manganese intake of less than 2 ug per day (inhalation and ingestion).

Based on the results of SAI's conservative exposure analysis, therefore, normal variations in daily intake of manganese (which range up to 7,000 ug per day) would be thousands of times greater than the maximum contribution of the Additive to

---

<sup>6/</sup> This assumption produces maximum ambient manganese concentrations due to use of the Additive essentially the same as those produced by the assumption that at least 30 percent of the manganese in the Additive is emitted.



-8-

manganese intake. An assumed maximum (worst case) manganese intake resulting from use of the Additive pales in comparison to:

- A multivitamin tablet (1,000-10,000 ug),
- An afternoon cup of tea (1,200 ug),
- A decision to eat a slice of whole wheat bread (334 ug) instead of white bread (164 ug), or
- Eating a banana (225 ug) instead of an apple (45 ug).

C. Impact of manganese on public health

Although neurotoxic effects are associated with exposures to manganese hundreds of thousand of times higher than maximum concentrations which would be caused by use of the Additive, manganese is still essential to human health. Such an anomaly is not unique to manganese. Other substances essential or beneficial to human health at relatively low levels (e.g., vitamin B-6) are neurotoxins at high exposure levels. The minute changes which the Additive would cause in current environmental levels of manganese would present no public health concern, a conclusion confirmed by numerous independent governmental reviews of the health implications of manganese emissions. For example,

- In 1985, EPA issued a final "Health Assessment Document for Manganese," and concluded that peak manganese concentrations as high as 125-250 ug/m<sup>3</sup> (concentrations higher than those at issue here by at least a factor of 10,000) would not "cause, or contribute to, air pollution which may reasonably be anticipated to result in an increase in mortality or an increase in serious illness."
- In September 1988, the Health Effects Institute (HEI) completed another independent review of the health literature on manganese, and HEI concluded that no adverse health effects (neurological or respiratory) would occur even at manganese emission levels one

-9-

hundred times higher than those that would result from use of the Additive.

- Based on its review of the health effects of manganese, the Canadian Department of National Health and Welfare concluded in 1978 that "there is no evidence at present to indicate that expected ambient manganese concentrations [from automobile exhaust] would constitute a hazard to human health."
- In 1986, the Royal Society of Canada again reviewed the health literature and concluded that "the general public has a wide margin of health safety with respect to the worst case use of MMT in gasoline."
- In 1987, an official from Australia's Department of Health completed an independent evaluation of the public health effects of manganese, and concluded that "there is no toxicological evidence to suggest that the increased level of airborne Mn resulting from combustion of MMT as a petrol additive is likely to constitute a health risk to the general population."
- Based on its review of the literature, the World Health Organization has concluded that an annual average concentration of  $1 \text{ ug/m}^3$  -- about ten to one hundred times higher than maximum urban ambient concentrations associated with use of the Additive -- "incorporates a sufficient margin of protection for the most sensitive population group."

To provide yet another independent scientific review of the health effects of manganese -- one which would incorporate studies performed since completion of the governmental reviews described above -- Ethyl retained Roth Associates, Inc. Dr. Roth and his colleagues (well-respected toxicologists and epidemiologists) have substantial experience regarding the public health impacts of various emissions, including manganese. They observed that:

- "Use of MMT [HiTEC® 3000] is unlikely to affect public health adversely. The anticipated increase of manganese in the environment from use of MMT is sufficiently small in comparison to the natural levels of this element and human intake of it that the body's

-10-

ability to maintain consistent manganese levels should be unaffected. Indeed, manganese is necessary for proper functioning of the human body. Thus, no effect on health would be anticipated. Data concerning the impact of exposure to manganese at the levels anticipated to follow approval of MMT are limited, but they are consistent with the lack of any adverse health effect."

- "[N]one of the three major issues raised by commenters [NIEHS, EDF, Dr. Herbert Needleman, Dr. John Donaldson, Mr. Everett Hodges] on the Ethyl application is valid. First, manganese is very different from lead chemically, biologically, and environmentally. Thus, the experience with lead as a gasoline additive cannot be used as a model of what will happen if MMT is added to gasoline. Second, while high levels of manganese are associated with neurological effects, concern that exposure to the far lower manganese levels expected to result from MMT use has no basis. Finally, the concern that manganese is associated with violent criminal behavior is essentially speculation. The one study that directly supports it is seriously flawed."
- "[N]one of the other concerns raised by [the same] commenters provide a sound basis for concluding that the addition of MMT to gasoline as proposed by Ethyl would endanger public health."

Ethyl, as well, asked the views of three other acknowledged experts regarding the health effects of manganese. Their responses:

- Dr. Henry M. Wisniewski (neuropathologist, expert on aging process, Director of Institute for Basic Research of N.Y. Department of Health): "Ethyl provided enough evidence to show that adding manganese will not negatively affect human health and environment . . . There is no evidence to suggest that [neurotoxic] effects take place at lower Mn levels . . . [The evidence] is clearly in favor of approving Ethyl's application."
- Dr. Robert Lauwerys (Professor of Industrial Toxicology and Occupational Medicine, Director of the Unit of Industrial Toxicology and Occupational Health at University of Louvain, Brussels): "[The World Health Organization's recommended guideline of 1 ug/m<sup>3</sup> average manganese exposure] "should incorporate a sufficient margin of protection for the most sensitive population

-11-

group." (Note: The Additive would result in ambient manganese levels 10 to 100 times less than 1 ug/m<sup>3</sup>.)

- o Dr. W. Clark Cooper (former Medical Director of U.S. Public Health Service): Following a 1984 comprehensive review of then-existing literature on public health implications of manganese in the environment, he concluded that the "minute increments of Mn that would result from the use of MMT as a gasoline additive should not have any impact on the public's health." Following a recent review of available literature, he stated that "[A]s of July 1990, I am not aware of any new evidence to alter the conclusions [of the 1984 review]; if anything they have been strengthened."

In sum, and contrary to concerns or allegations expressed by a few of the commentators on Ethyl's waiver application, extensive studies and research have been made on the health effects of manganese. An informed body of opinion clearly agrees, without reservation, that the small levels of manganese emissions associated with use of the Additive would present no public health concern. The real public health effect of the Additive would be positive -- significant reductions in NOx, CO, reactive HC, benzene, and formaldehyde.

**II. SUPPLEMENTAL INFORMATION CONFIRMS THAT THE ADDITIVE WILL NOT CAUSE OR CONTRIBUTE TO THE FAILURE OF EMISSION CONTROL DEVICES, AND THAT THE ADDITIVE IS AN ATTRACTIVE OPTION FOR POLLUTION CONTROL.**

- A. Use of the Additive Will Enhance Catalytic Efficiency Without Causing Plugging or Other Adverse Effects on Emission Control Systems.

In order to supplement the extensive test results in its waiver application, Ethyl is submitting herewith further information and enclosures on the Canadian experience regarding the effect of the Additive on catalysts. For example,

-12-

- The Royal Society of Canada concluded in 1986 that "in eight years of use of MMT in unleaded gasoline in Canada there does not appear to have been a higher incidence of catalytic converter failure than in the United States."
- The Canadian Government Specifications Board (CGSB) reported in 1986 that "use of MMT at current CGSB levels does not significantly compromise emission-control system operation or component durability."
- Both the Motor Vehicle Manufacturers Association and the Automobile Importers of Canada reported to the CGSB in 1986 "that manufacturers' Canadian warranty claims on emission components are comparable to the U.S.," where the Additive is not used in unleaded gasoline.
- Petro-Canada, Inc., an oil company wholly owned by the Canadian government, has reported in 1990 based on an ongoing investigation that "[w]e have not had a single complaint referencing catalyst plugging . . . . [O]ur research department has examined a number of catalysts from our high-mileage in house test fleet without finding evidence of catalyst plugging . . . . [A]uto manufacturers . . . have not submitted any evidence that MMT is associated with catalyst plugging."

The only study of which Ethyl is aware that suggests the Additive would cause catalyst plugging under normal driving conditions was outlined in a paper presented at an SAE meeting recently by Ford Motor Company. That study, however, is flawed in several critical respects, most notably because the catalyst conversion efficiencies reported by Ford were based on laboratory methods for which no correlation with actual field emissions testing is shown. By contrast, Ethyl's extensive test program demonstrated in actual operations after 75,000 miles of vehicle operation (and beyond) that use of the Additive did not adversely affect the catalyst, and in fact, improved the conversion efficiency for NOx emissions.

-13-

The record fully supports Ethyl's conclusion that the Additive will not cause catalyst plugging.

**B. Effects of the Additive on NOx and CO Emissions**

In response to questions raised at the public hearing, Ethyl contacted Dr. Roy Harrison, the Director of the Institute of Aerosol Science at the University of Essex in England, regarding the effects of the Additive on NOx and CO emissions. Based on his research addressing such effects, Dr. Harrison has offered comments (which are enclosed) explaining, from a theoretical standpoint, the reason significant reductions in NOx and CO emissions should be anticipated.

**C. Compatibility of the Additive with Oxygenates**

Ethyl is submitting herewith additional information showing that the Additive will complement the use of oxygenates, not replace them. With the anticipated limitations on the aromatic content of gasoline, both oxygenates and the Additive will be needed to provide required octane levels.

**D. Compliance with More Stringent Mobile Source Standards**

As Ethyl showed in its waiver application, use of the Additive would not adversely affect compliance with even tighter HC emission standards, as proposed in the pending Clean Air Act legislation. Indeed, Ethyl's supplemental analyses show that the reactivity of HC emissions would be significantly reduced with use of the Additive, and that catalytic converter efficiency would increase for CO and NOx while remaining constant for HC.

-14-

By replacing aromatics, improving overall converter efficiency, and reducing the reactivity of HC emissions, the Additive could assist in the attainment of future mobile source standards, including more stringent HC standards.

### III. CONCLUSION

The information presented in Ethyl's waiver application, as supplemented by these comments, demonstrates that use of the Additive would not cause or contribute to the failure of emission control systems to meet applicable emission standards, and would promote the overall objectives of the Act. The Additive would provide a significant health benefit by substantially reducing mobile source emissions of pollution. It would not perceptibly change environmental loadings of manganese. It would pose no threat whatsoever to the public health of the nation. And it would reduce this nation's dependence on imported oil. For all of these reasons, this waiver application should be promptly approved.

# TABLE OF CONTENTS

I.	INTRODUCTION . . . . .	1
II.	THE HEALTH INFORMATION SUBMITTED BY ETHYL IN ITS WAIVER APPLICATION AND IN THESE SUPPLEMENTAL COMMENTS FULLY JUSTIFIES APPROVAL OF THE APPLICATION . . . . .	3
A.	The Statutory Standard . . . . .	5
B.	Ethyl Has Satisfied the Statutory Standard. . . . .	9
III.	USE OF THE ADDITIVE WILL HAVE A BENEFICIAL EFFECT ON PUBLIC HEALTH, WELFARE, AND THE PRODUCTIVE CAPACITY OF THE NATION. . . . .	12
A.	Use of the Additive Reduces Emissions of Criteria and Other Pollutants. . . . .	13
B.	While Reducing Emissions of Numerous Noxious Pollutants, Use of the Additive Will Not Significantly Change Existing Levels of Manganese Exposure -- Levels that EPA and Other Independent Organizations Have Concluded Present No Public Health Concern. . . . .	19
1.	Manganese emissions resulting from use of the Additive. . . . .	19
2.	Use of the Additive will not significantly change environmental levels of manganese. . . . .	23
a.	Ambient air . . . . .	23
b.	Soil . . . . .	26
4.	Given the small contribution of manganese to the air and soil, use of the Additive will not discernibly change the public's exposure to manganese. . . . .	29
5.	Concentrations of manganese in the environment associated with use of the Additive will not adversely affect the public health or welfare. . . . .	31
a.	Governmental reviews of manganese health effects . . . . .	32



b.	None of the comments raised at the public hearing or in comments to date cast any doubt on the continuing validity of the unanimous findings of the HAD and the other independent governmental reviews that low level manganese concentrations present no public health concern. . . . .	37
C.	Ambient Exposure to the HiTEC 3000 Additive Does Not Present a Public Health Risk. . . . .	44
D.	Use of the Additive Will Promote the Overall Objectives of the Act. . . . .	46
IV.	USE OF THE ADDITIVE WILL ENHANCE CATALYTIC EFFICIENCY WITHOUT CAUSING PLUGGING OR OTHER ADVERSE EFFECTS ON EMISSION CONTROL SYSTEMS. . . . .	47
A.	The Change in Emissions Associated with Use of the Additive is Attributable to the Catalytic Properties of Mn3O4. . . . .	48
B.	Use of the Additive Will not Cause Plugging of Catalytic Converters. . . . .	49
C.	Use of the Additive Will Complement the Use of Oxygenates, Not Replace Them. . . . .	52
D.	Use of the Additive Will Not Adversely Affect Compliance with Tighter Hydrocarbon Emission Standards Adopted in the Future. . . . .	54
V.	<u>CONCLUSION</u> . . . . .	57

-iii-

APPENDICES

- Appendix 1 -- Reactivity of Hydrocarbon Emissions
- Appendix 2 -- Manganese: Environmental Levels and Population Exposure
- Appendix 3 -- H.D. Roth, et al., Analysis of Health Risk from the Addition of HiTEC-3000 to Unleaded Gasoline at a Concentration of 0.03125 Grams Manganese Per Gallon of Gasoline (July 1990)
- Appendix 4 -- Methylcyclopentadienyl Manganese Tricarbonyl (MMT): An Assessment of the Human Health Implications of its Use as a Gasoline Additive, Canadian Minister of National Health and Welfare (1978)
- Appendix 5 -- The Royal Society of Canada, Lead in Gasoline: Alternatives to Lead in Gasoline, The Commission on Lead in the Environment (1986)
- Appendix 6 -- Letter from the National Health and Medical Research Council of Australia
- Appendix 7 -- Assessments of Manganese and the Public Health by Independent Health Experts
- Appendix 8 -- Coe, et al., Determination of Methylcyclopentadienyl Manganese Tricarbonyl by Gas Chromatography - Atomic Absorption Spectrometry at  $\text{ng m}^{-3}$  Levels in Air Samples, Analytica Chimica Acta, 120 (1980) 171-176
- Appendix 9 -- R.M. Harrison, The Influence of  $\text{Mn}^{304}$  from MMT Combustion on Gasoline Vehicle Emissions (1990)
- Appendix 10 -- An Assessment of the Effect of MMT on Light-Duty Vehicle Exhaust Emissions in the Canadian Environment, Canadian Government Specifications Board (1986)
- Appendix 11 -- Ethyl Corporation, Characterization of Automotive Catalyst Exposed to the Fuel Additive MMT, Comments on SAE Paper 890582 (1989)

I. INTRODUCTION

On May 9, 1990, Ethyl Corporation ("Ethyl") filed a fuel additive waiver application under § 211(f)(4) of the Clean Air Act ("CAA" or "Act") for use of the HiTEC® 3000 Performance Additive (the "Additive") at a concentration of 0.03125 grams manganese per gallon as the Additive in unleaded gasoline. On June 5, 1990, the Environmental Protection Agency ("EPA" or "Agency") published a notice in the Federal Register indicating that it intended to hold a public hearing on the waiver application and would accept comments on the waiver until July 22, 1990.<sup>1/</sup>

Since submittal of the waiver application, and at the public hearing, a limited number of comments have been submitted to the Agency concerning the waiver application. This submittal responds to those comments. If any additional questions are raised in comments received on or about July 23, 1990, Ethyl will respond to them as expeditiously as possible.

As noted in Ethyl's initial submission, the principal burden Ethyl must meet under CAA § 211(f)(4) is to show that use of the Additive will not cause or contribute to the failure of emission control systems to meet applicable emission standards. Ethyl believes that its comprehensive fuel additive test program and the materials presented in its waiver application satisfy this burden. To date, no commentator has submitted any analysis or new data refuting this conclusion.

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<sup>1/</sup> 55 Fed. Reg. 22347 (June 5, 1990). Because July 22, 1990 falls on a Sunday, EPA informally indicated that they would accept as timely comments filed by July 23, 1990.

-2-

In addition, Ethyl provided in its waiver application information showing that approval of the application would further the general purposes of the Act -- i.e., that it would promote the "public health," the public "welfare," and the "productive capacity" of the nation. Ethyl did so by addressing, among other things, the overall impact of the Additive on exposure to emissions of both regulated pollutants (such as nitrogen oxides, carbon monoxide, hydrocarbons, and benzene) and manganese.

The initial submission showed that EPA and other independent scientific bodies have unanimously concluded that low levels of manganese emissions present no public health concern, and that the overall impact of the Additive on public health would be positive. Ethyl also showed that use of the Additive would promote the "productive capacity" of the nation.

Several commentators have now suggested that Ethyl has not provided enough information upon which to make a determination that use of the Additive will not adversely affect the public health. The principal focus of these supplemental comments is, therefore, on the public health implications associated with use of the Additive. These comments also briefly address several issues that have been raised in connection with the impact of the Additive on emission control devices.

II. THE HEALTH INFORMATION SUBMITTED BY ETHYL IN ITS WAIVER APPLICATION AND IN THESE SUPPLEMENTAL COMMENTS FULLY JUSTIFIES APPROVAL OF THE APPLICATION.

As noted above, several comments have been submitted to the Agency suggesting that Ethyl has not adequately addressed the public health implications of the Additive.<sup>2/</sup> None of these comments, however, contest that the Additive will benefit public health by reducing emissions of nitrogen oxide ("NOx") and carbon monoxide ("CO"), by reducing the reactivity of hydrocarbon ("HC") emissions, and by lowering emissions of other pollutants, such as benzene and formaldehyde.

Rather, these comments merely express a generalized concern that, since manganese is a neurotoxin at high exposure levels, the very small increases associated with use of the Additive (levels within the range of normal background concentrations) should be of public concern.<sup>3/</sup> These comments provide no evidence that any adverse effects in fact are likely to occur at low exposure levels. As a result, these comments do no more than (1) complain that Ethyl should provide more evidence that alleged health effects will not occur, and (2) argue that, in the absence of further evidence, the hypothetical health effects alleged

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<sup>2/</sup> See, e.g., Transcript of Public Hearing on Ethyl Corporation Fuel Waiver Application, U.S. Environmental Protection Agency, pp. 6-15, 42-43 and 63-64 (June 22, 1990)[hereinafter "Transcript"].

<sup>3/</sup> See, e.g., id. at p. 7.

-4-

should be given more weight than the real benefits associated with use of the Additive.<sup>4/</sup>

As discussed above, these commentators have presented an alarmist's view of alleged potential health effects of manganese exposure which is inconsistent with the existing, extensive, and widely-accepted body of evidence addressing manganese. Moreover, they have simply ignored the real and significant public health benefits that would be associated with use of this Additive. As discussed below, since these commentators lack proof of the effects they allege, they improperly attempt to assign to Ethyl the burden of disproving their unfounded allegations. This is a burden not contemplated by CAA § 211(f)(4).<sup>5/</sup>

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<sup>4/</sup> See, e.g., id. at p. 17. It should be noted that these commentators are simply wrong when they state that Ethyl has made no attempt to address the public health effects of manganese. See, e.g., id. at pp. 64-65. Ethyl's waiver application and an appendix to the application both address this issue. See In Re Application for a Fuel Additive Waiver Filed by Ethyl Corporation Under § 211(f)(4) of the Clean Air Act (May 9, 1990) [hereinafter "Waiver Application"] at pp. 67-69, and Appendix 8 thereto. Ethyl did not feel it was necessary, however, to describe in detail the comprehensive reviews of the health implications of manganese already performed by EPA, the Canadian government, Australia, the World Health Organization and the Health Effects Institute. Moreover, contrary to the contentions of these commentators, Ethyl's waiver application and the materials on which it relies address the neurotoxic effects of manganese. See, e.g., Waiver Application, Appendix 8, at p. 11; Health Assessment Document for Manganese (hereinafter "HAD"), at 6-4 to 6-46. A copy of the HAD is provided in Appendix 3 as Attachment B-1.

<sup>5/</sup> Indeed, the Agency itself acknowledges that Congress did not intend waiver applicants to bear the burden of proving "negative proposition[s]" under § 211(f)(4). See Waiver Application at p. 43, n. 100 and accompanying text.

-5-

A. The Statutory Standard

The statutory standard for judging fuel additive waiver applications under the Act does not specifically address the public health-related implications of use of a new additive. Section 211(f)(4) of the Act provides only that an applicant for a fuel additive waiver must show that the additive

will not cause or contribute to a failure of any emission control device or system (over the useful life of any vehicle in which such device or system is used) to achieve compliance by the vehicle with the emission standards with respect to which it has been certified.<sup>6/</sup>

There is nothing in the relevant statutory language which refers directly to public health and welfare.

Nor, for that matter, does the legislative history of § 211(f) identify health as a relevant criterion. The legislative history makes clear that Congress was concerned primarily with the impact of new fuel additives on emission control systems. One congressional report on the 1977 Amendments to the Act indicates, for example, that Congress enacted § 211(f) "to prevent the untested use of additives with cavalier disregard for harmful effects on emission control systems and devices."<sup>7/</sup> Similarly, another report indicates that § 211(f) was enacted because "emission systems currently in use could not be

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<sup>6/</sup> 42 U.S.C. § 7545(f)(4).

<sup>7/</sup> A Legislative History of the Clean Air Act Amendments of 1977, Comm. Print, Senate Comm. on Env't and Public Works 1978) (Serial No. 95-16), at 362 (hereinafter "1977 Legis. Hist.").

-6-

adequately protected from possible deterioration" due to the use of new additives by then-existing law.<sup>8/</sup> Indeed, the only reference to public health in the legislative history of § 211(f) makes clear that Congress did not intend that the Agency's decisions under § 211(f)(4) be governed by health-related issues.<sup>9/</sup>

This interpretation of § 211(f) has been adopted by the Agency in prior waiver application decisions. In one of EPA's first decisions under § 211(f)(4), the Petro-Tex Chemical Corporation requested a waiver for the use of MTBE in unleaded gasoline. In denying the waiver application on the basis of an insufficient record regarding MTBE's impact on evaporative and exhaust emissions, EPA noted that:

Aldehyde emissions have been widely discussed in connection with the use of oxygenated fuels. Although emissions of aldehyde, and other unregulated pollutants are of continuing interest to EPA due to their potential adverse effect on health, they have

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<sup>8/</sup> Id. at 1464 (emphasis added).

<sup>9/</sup> "The committee expects the Administrator to require manufacturers to test registered additives insofar as they affect health and public welfare under sections (a), (b) and (c) of this section." 1977 Legis. Hist. at 1466 (emphasis added). These other provisions of § 211 therefore are to be the principal vehicle for considering public health concerns with respect to fuel additives.

In this regard, it should be noted that the Additive has been a registered fuel additive since the early-1970s. No one has raised any public health concern with respect to use of this Additive under any of these other provisions of the Act. Similarly, no one has ever challenged EPA's final determination under § 112 of the Act that manganese cannot be reasonably anticipated to cause or to contribute to serious health effects. See infra pp. 11-12.



-7-

no bearing on this waiver decision. The waiver provision, section 211(f)(4), is solely concerned with the emission standards which apply to tailpipe emissions of HC, CO, and NOx and evaporative HC emissions.<sup>10/</sup>

This interpretation of § 211(f)(4) is also reflected in the Agency's waiver application guidelines. These guidelines describe the information that a fuel additive waiver applicant must submit to the Agency for its review. While the guidelines direct the applicant to submit, among other things, "data relating to a fuel additive's emissions effects which are derived from vehicle testing," they make no reference to information on the potential public health implications of a new Additive.<sup>11/</sup>

While § 211(f)(4) does not require the Agency to address public health, however, this does not mean that public health has no relevance to a waiver proceeding. When it amended the Act in 1970, Congress stated that the overall goal of the Act is "to protect and enhance the quality of the Nation's air" in a way that "promote[s] the public health and welfare and the productive capacity of its population."<sup>12/</sup> As the Agency has recognized, a "balancing of the social and economic considerations with the environmental implications [of a decision is necessary] . . . to fulfill the mandate of the Clean Air Act to 'protect and enhance

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<sup>10/</sup> In Re Application for MTBE, Decision of the Administrator (December 26, 1978) at 4, n. 5. EPA also indicated that "[n]otwithstanding section 211(f), EPA retains authority to regulate any fuel or fuel additive under section 211(c) of the Act." Id. (Emphasis added).

<sup>11/</sup> See 43 Fed. Reg. 11258 (1978).

<sup>12/</sup> See 42 U.S.C. § 7401(b)(1).

the quality of the Nation's air resources so as to promote the public health and welfare and the productive capacity of its population.<sup>13/</sup> The courts have expressly recognized that the mobile source provisions of Title II should be implemented in light of these broader goals of the Act.<sup>14/</sup>

While the applicant clearly has a special burden under § 211(f)(4) to meet the "cause or contribute" standard with respect to emission control devices, nothing in the statutory language or legislative history of this provision extends this special burden to other issues, such as public health considerations, made relevant by the general purposes clause of the Act.<sup>15/</sup> As a result, the only "burden" Ethyl must carry concerning the Additive's impact on public health is the burden of coming forward with sufficient information for the Agency to exercise a reasoned judgment regarding the overall health effects of the Additive.<sup>16/</sup>

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<sup>13/</sup> 39 Fed. Reg. 31000, col. 1 (1974) (emphasis added).

<sup>14/</sup> In Chrysler Corp. v. U.S. Environmental Protection Agency, 631 F.2d 865, 888 (D.C. Cir. 1980), for example, the court refused to interpret the automotive recall provision of section 207 of the Act "in a manner which runs counter to the broad goals which Congress intended it to effectuate." The court acknowledged that the "broad purpose of the Clean Air Act Amendments of 1970 is plain: 'to protect and enhance the quality of the Nation's air resources so as to promote the public health and welfare and the productive capacity of its population[.]'" Chrysler Corp., 631 F.2d at 888. See also General Motors Corp. v. Ruckelshaus, 742 F.2d 1561, 1572 n.15 (D.C. Cir. 1984).

<sup>15/</sup> See supra note 6, and pp. 5-7.

<sup>16/</sup> Where Congress made public health considerations a principal factor in regulatory decisions regarding fuel additives, Congress  
(continued...)

-9-

B. Ethyl Has Satisfied the Statutory Standard.

Given the overall purposes of the Act, Ethyl specifically addressed in its waiver application the implications of the use of the Additive for public health and welfare, and for the productive capacity of the Nation. On the public health issue, for example, Ethyl presented information on the public health effects of manganese, citing, among other things, the results of studies conducted by the United States and other governments regarding the effects of manganese in the environment. At the same time, Ethyl showed that the substantial reduction in overall automotive tailpipe emissions associated with use of the Additive

<sup>16/</sup> (...continued)

placed an affirmative burden on the Agency to determine based on available evidence that an additive will adversely affect the public health. CAA § 211(c). Section 211(c)(1) of the Act provides, in pertinent part, that:

The Administrator may, from time to time . . . by regulation, control or prohibit the manufacture, introduction into commerce, offering for sale, or sale of any fuel or fuel additive for use in a motor vehicle engine (A) if in the judgment of the Administrator any emission product of such fuel or fuel additive causes, or contributes, to air pollution which may reasonably be anticipated to endanger public health or welfare . . . . 42 U.S.C. § 7545(c)(1).

Under the terms of this provision, the Agency is "free to regulate . . . [a] fuel additive under section 211" only after it considers "all relevant medical and scientific evidence available," id. at § 7545(c)(2)(A), and then determines that the additive "may reasonably be anticipated to endanger public health and welfare." See, e.g., Ethyl Corp. v. EPA, 541 F.2d 1, 11-33 (D.C. Cir.), cert. denied, 426 U.S. 941 (1976); Amoco Oil Co. V. EPA, 501 F.2d 722 (D.C. Cir. 1974).